THE ELECTRONIC STRUCTURE OF THE GROUND STATE OF THE CARBON ATOM

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Dedicated

to my parents

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INTRODUCTION

In the last decade, much effort has been devoted to the obtaining of accurate, non-relativistic, Hartree-Fock (HF) representations of atomic wave functions.(1-5) For closed shell systems, these consist of a single, energy optimized, Slater determinant made up of symmetry adapted spin-orbitals. For most open shell cases, more than one determinant is necessary in order to satisfy the symmetry requirements of the L, S multiplets.

The HF method is useful for a large variety of purposes,(6, 7) such as to obtain a qualitative and quantitative description of optical and X-ray spectra, or to evaluate certain one-electron properties (electronic density distributions, diamagnetic susceptibilities, atomic scattering factors, etc.). In addition, the HF solutions serve as excellent starting points for improved calculations.

The accurate computation of quantities like transition probabilities,(8, 9) inelastic scattering differential cross sections, binding energies of molecules,(10) electron affinities of neutral systems,(11, 12) hyperfine structure constants, etc., and the proper understanding of phenomena related to these, however, require the use of wave functions beyond the HF approximation. In most of these cases, a good calculation provides a test, not only for the experimental methods, but also for the theory itself.

The two standard variational methods for improving the HF solutions are: (i) the interparticle method, in which the expansion of the wave function Ψ includes the interparticle coordinates r_{ij} explicitly, (13, 14) and (ii) the configuration interaction (CI) method, in which Ψ is expanded in terms of properly symmetrized products of one-electron functions. (15, 16) Both have been proved useful in atomic and molecular calculations, the first one, because of its potential accuracy, the second one because it is easy to handle, to interpret, and to extend for larger systems.

The aspects involved in the determination of N-electron Ψ 's where N equals or is greater than four, are of an essentially different nature in the two methods. In the interparticle formalism, the problems arising in the evaluation of the integrals and in the obtaining of appropriate computer codes to handle the complicated indexing involved in the calculation of the Hamiltonian matrix, are not entirely solved yet. (17, 18) On the contrary, there are no more real numerical or programming difficulties in non-relativistic CI calculations, (19, 20) and, so, at the present time CI is the most promising alternative. In this work, we obtain and analyze an accurate CI wave function for the ground state of the carbon atom.

Chapters I through IV are of a general nature; they concern the theory behind the procedure used in this calculation, which is applicable to all first row atoms as well: we describe in detail the optimization of the parameters of the Slater type orbitals (STO's), the use of first order density matrices of selected CI wave functions to obtain the one-electron basis, the introduction of the whole degenerate space of each configuration into the CI expansion, and the means to partition it to improve the convergence of that expansion.

The calculation of the ^3P state of the carbon atom is described in Chapter V. In Chapter VI the results are discussed and compared with other works in the literature.

CHAPTER I

THE CONFIGURATION INTERACTION EXPANSION

1.1 The Method of Configuration Interaction

Let $\{\psi_k\}$ be a complete and orthonormal set of one-electron functions of the space-spin coordinate $x = (\vec{r}, \xi)$. For an N-electron system, for every selection of N indices $k_1 < k_2 < \ldots < k_n$, one can define a normalized Slater determinant D_i:

$$D_i\,(x_1, x_2, \ldots, x_N) = (N!)^{-\frac{1}{2}} \det \{\psi_{k_1}(x_1)\;\psi_{k_2}(x_2) \ldots \psi_{k_n}(x_N)\}.$$

It can be easily proved (16) that every normalizable antisymmetric wave function can be expressed as a linear combination of Slater determinants built up from a complete basic set of one-electron functions. In the method of configuration interaction (CI), the exact wave function is hence written as

$$\Psi(x_1, x_2, \ldots, x_N) = \Sigma_i\; D_i\,(x_1, x_2, \ldots, x_N)\; c_i\;.$$

The coefficients c_i are determined variationally, as those which minimize the total energy E :

$$E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle = \Sigma_{ij} H_{ij} c_i^* c_j / \Sigma_{ij} c_i^* c_j \ ,$$

where $H_{ij} = \langle D_i | H | D_j \rangle$ is the matrix element of the total Hamiltonian H between the basic Slater determinants D_i and D_j . The condition for the energy to be an extremum, $\delta E = 0$, leads to the well-known matrix eigenvalue equation

$$(\mathbb{H} - E\,\mathbb{1})\,\mathbb{c} = 0 \ ,$$

which has non-trivial solutions only for values of E which are roots of the secular equation

$$\det(\mathbb{H} - E\,\mathbb{1}) = 0 \ .$$

For a complete set of one-electron functions, this equation is of infinite dimension, and cannot be solved unless it is truncated. What is done in practice is to choose a good, small one-electron set $\{\Phi_i(1);\ i = 1, 2, \ldots, M \geq N\}$. The finite CI expansion consisting of all possible Slater determinants formed with $\{\Phi_i\}$, is called a full CI expansion. Both the eigenfunctions and the eigenvalues of the full $\mathbb{H}$ matrix are invariant under non-singular linear transformations (n. s. l. t.'s) of the set $\{\Phi_i\}$ because, in this case (sufficient condition), such transformations are equivalent to n.s.l.t.'s of the set of N-electron determinants. It is possible to find a n.s.l.t. of the original set, which optimizes the convergence of the full CI: this is discussed in Chapter II. A practical definition of optimum convergence is given in Section 3.4.

1.2. Projection Operators

For an atom, the non-relativistic Hamiltonian H may be written as

$$H = \Sigma_i h_i + \Sigma_{i<j} g_{ij}$$

where

$$h_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i}$$

$$g_{ij} = \frac{1}{r_{ij}} \quad ;$$

the mass polarization terms have been neglected, and atomic units (a.u.) are used throughout.

This Hamiltonian has certain symmetry properties which may best be taken advantage of by using them to transform the set of N-electron functions $\{D_i\}$ into a more convenient set $\{\Phi_i\}$ of symmetry adapted functions. Such a set may be obtained by means of projection operators;$^{(16, 21, 22)}$ it is much smaller than $\{D_i\}$

because it spans only that part of the Hilbert space with a certain symmetry type.

The Hamiltonian H defined above, commutes with the operators L^2, S^2, L_z, S_z (squares and z-components of the total orbital and spin angular momenta), and with $\mathbb{P}$, the parity operator. Let us denote by Λ any one of these operators. Then, for non-degenerate states Ψ ,

$$\Lambda \Psi = \lambda_k \Psi$$

meaning that the total wave function Ψ is an eigenfunction of Λ with eigenvalue λ_k. The corresponding projection operator O_k^Λ is defined by the property

$$O_k^\Lambda \Phi = \Phi_k \quad \text{or} \quad 0 \qquad ,$$

where Φ is a normalizable arbitrary function, and Φ_k satisfies

$$\Lambda \Phi_k = \lambda_k \Phi_k$$

An explicit expression for O_k^Λ is given by Löwdin: (16)

$$O_k^\Lambda = \prod_{l \neq k} (\Lambda - \lambda_l) / (\lambda_k - \lambda_l) \qquad ; \qquad (1.1)$$

since Λ commutes with H, so does O_k^Λ. In addition, O_k^Λ satisfies the relations:

$$(O_k^\Lambda)^2 = O_k^\Lambda = (O_k^\Lambda)^\dagger$$

$$O_k^\Lambda O_l^\Lambda = 0 \quad \text{for} \quad k \neq l \,.$$

1.3. Projected Configurations

The one-electron functions are taken to be symmetry adapted spin-orbitals $\psi_{i\ell m_\ell m_s}$ of the form

$$\psi_{i\ell m_\ell m_s} = R_{i\ell}(r)\, Y_{\ell m_\ell}(\theta, \varphi)\, \xi_{m_s}(\sigma_s)$$

where the $Y_{\ell m_\ell}(\theta, \varphi)$'s are normalized spherical harmonics,(23) the $\xi_{m_s}(\sigma_s)$'s are the spin functions α or β, and the $R_{i\ell}(r)$'s are linear combinations of STO's, $S_{j\ell}$:

$$R_{i\ell} = \sum_{j}^{J(\ell)} S_{j\ell}\, a_{j\ell i}$$

$$S_{j\ell} = N_{j\ell}\, r^{(n_j + \ell)}\, e^{-Z_{j\ell} \cdot r}$$

$$N_{j\ell} = [(2Z_{j\ell})^{[2\ell + 2n_j + 3]} / (2\ell + 2n_j + 2)!\,]^{\frac{1}{2}}$$

the $R_{i\ell}$'s being orthonormal among themselves for each ℓ value.

Let us now define a configuration as an ordered set of N indices (i, ℓ) associated with the spin-orbitals $\psi_{i\ell m_\ell m_s}$. To each pair of (i, ℓ) indices there correspond many (in fact, $4\ell + 2$) different spin-orbitals. Hence, one can form several Slater determinants $D_{K\alpha}$ belonging to each configuration K and, since the spin-orbitals are symmetry adapted, the determinants are eigenfunctions to L_z, S_z, and parity. In addition, it is possible to form certain linear combinations Φ'_K of determinants belonging to the same configuration K, such that the Φ'_K's are eigenfunctions to L^2 and S^2: we shall call them projected configurations. When only one linearly independent Φ'_K can be obtained, the configuration K is said to be non-degenerate in the corresponding L, S state. Otherwise, a superscript (p) is introduced to label the various projected functions, $\Phi'^{(p)}_K$, and K is then called g_K-degenerate.

The projected configurations are symmetry adapted N-electron functions; besides, it is convenient to orthonormalize them. The orthonormal set $\{\Phi^{(p)}_K\}$ of eigenfunctions to L^2, S^2, L_z, S_z, and $\mathbb{P}$, can then be used as a basis in which to expand the total wave function Ψ of the same symmetry type:

$$\Psi = \Sigma_{Kp} \; \Phi^{(p)}_K \; a_{Kp} \quad . \tag{1.2}$$

The $\Phi^{(p)}_K$'s are called terms of the CI expansion. They are obtained by applying the projection operator

$$O_{L,S}^{L^2,S^2} = O_L^{L^2} \cdot O_S^{S^2} \tag{1.3}$$

upon the determinants $D_{K\alpha}$, and then orthogonalizing successively the resulting functions. They can be expressed as

$$\Phi_K^{(p)} = O_{L,S}^{L^2,S^2} [\sum_{\alpha=1}^{p} D_{K\alpha} b_{K\alpha}^{(p)}] = \sum_{\alpha=1}^{n_K} D_{K\alpha} c_{K\alpha}^{(p)} \tag{1.4}$$

where n_K is the number of determinants which span configuration K.

In the basis $\{\Phi_K^{(p)}\}$, the matrix elements $H_{KL}^{(pq)}$ of the Hamiltonian are:(21)

$$\begin{aligned} H_{KL}^{(pq)} &= \langle \Phi_K^{(p)} | H | \Phi_L^{(q)} \rangle \\ &= \sum_{\alpha=1}^{p} \sum_{\beta=q}^{n_L} b_{K\alpha}^{(p)} c_{L\beta}^{(q)} \langle D_{K\alpha} | H | D_{L\beta} \rangle , \end{aligned} \tag{1.5}$$

where we have used the "turn-over" rule and Eq. (1.4). The turn-over rule is assumed to be applied in the most efficient way, i.e.

$$g_K \cdot n_L \le g_L \cdot n_K \quad .$$

The integrals $I_{\alpha\beta}$

$$I_{\alpha\beta} = \langle D_{K\alpha} | H | D_{L\beta} \rangle$$

are evaluated as described in Reference 23. The calculation of the $b_{K\alpha}^{(p)}$ and $c_{K\alpha}^{(p)}$ coefficients is discussed in Reference 20.

1.4. Classification of the Configurations

The introduction of symmetry adapted spin-orbitals permits a classification of configurations into classes and subclasses. A class is defined by the particular partition of N among the spin-orbitals of different ℓ values. Within each class, a subclass is defined by the particular set of partitions of the quantum number i among the spin-orbitals with the same ℓ value. Thus, the subclasses $(s_w)^2 s_x (p)^2 d$, $s_w s_x s_y (p)^2 d$, $(s_w)^2 s_x p_u p_t d$, and $s_w s_x s_y p_u p_t d$, form the class (3s, 2p, 1d). Under linear transformations of the $R_{i\ell}$ functions, a given configuration is transformed into other configurations of the same class. A full CI expansion over a given class is invariant under n.s.l.t.'s of the $R_{i\ell}$'s, provided the whole degenerate space of each configuration is considered. This is, however, a sufficient but not necessary condition, since if only a few couplings - but the same for all configurations of a class - of spin and orbital angular momenta are introduced in the CI expansion, the latter is also invariant under a general n.s.l.t. of the $R_{i\ell}$'s. Finally, some special n.s.l.t.'s can be found, under which certain truncated CI expansions remain invariant; these are used in the selection of the one-electron basis (see Chapter II), with the purpose of improving the rate of convergence of Ψ .

CHAPTER II

THE BASIC ONE-ELECTRON FUNCTIONS

Any complete set of one-electron functions can be used as a basis for the CI expansion, and, as long as the latter extends over the complete set, the exact Ψ shall be obtained. In practice, however, it is important to obtain a set such that only a few terms provide a relatively accurate Ψ. In this calculation, a great deal of care has been given to the selection of the basic spin-orbitals.

The HF approximation for closed shell systems consists of only one Slater determinant. When it is used as the zeroth-order wave function, all the other determinants in the CI expansion can be classified as one-, two-,..., n-excited determinants, according to how many spin-orbitals differ from those in the HF solution. For non-closed shell systems, where the HF wave function may be a linear combination of determinants, each new determinant is classified as above with respect to the HF determinant it differs less from. Let us point out here the difference between n-excited determinants and n-excited configurations (or n-excitations), the latter being defined as configurations differing from the HF one by n sets of (i, ℓ) indices.

It is also customary to define the correlation energy E_{corr}, as the difference between the exact non-relativistic energy E_{nr} and the HF energy E_{HF}:(16)

$$E_{corr} = E_{nr} - E_{HF} \quad .$$

According to the many-electron theory,(24) the HF wave function is a good starting point for better approximations, because it has the formal role of making the rest of the exact Ψ and E come out simple: the CI expansion consists then mainly, of HF and two-excited determinants, while the correlation energy is approximated as the sum of the correlation energies of all the possible pairs of electrons. In Section 2.4, we concentrate on obtaining a fast convergence of the expansion in two-excited determinants. Some one-excited ones are quite important, but they are very few, and hence do not constitute a practical problem. The convergence of the remainder of the CI series, which consists essentially of three- and four-excited determinants, is directly related to the above, as will be discussed in Section 5.6.

2.1. Initial Set of One-Electron Functions

We start then with HF spin-orbitals from a nominal HF wave function,(25) i.e. one which is intermediate in accuracy between the minimal STO set and the saturated HF wave functions, but which gives an energy closer to that obtained from the latter one. For the first row atoms, the nominal HF set consists of a small (4s, 3p) STO basis. Thus, four s-type and three p-type orbitals can be formed from it: the HF orbitals are known; the others are found by successive Schmidt orthonormalization of linear combinations of STO's. A CI calculation including all the single and double excitations which can be formed from this one-electron basis yields a preliminary CI wave function.

The second step is to increase the STO basis. The experience of many workers$^{(26, 27)}$ points to the fact that, when an HF solution is used as the zeroth-order wave function, the pair correlations are localized largely within a shell and between electrons in the same immediate region of space. It seems hence reasonable to look for new STO's giving rise to orbitals which are optimum for expanding the double excitations of a pair of HF spin-orbitals. However, this requires the obtaining of a large number of STO's: for example, one of each ℓ-symmetry type for every pair; furthermore, many of them have large approximate linear dependencies among themselves, and this introduces appreciable errors in the calculation of the integrals. What is done, then, is to optimize several STO's per shell, first in the L shell because it is known to be the most difficult one, then in the K shell and Intershell alternatively; within each of these, the STO'S are considered in order of expected importance. In order to select a new STO one chooses, out of various sets of parameters $(n_j;Z_{j\ell})$, the one which yields the best CI energy. For optimization purposes, the CI expansion for each shell includes single and double excitations alone, and, in the case of degenerate configurations, only the energy relevant terms, as deduced from preliminary calculations.

Within each shell and ℓ-symmetry type, "saturation" with STO's is achieved when no new STO can be found, which gives any substantial improvement in the energy (this, of course, depends on the particular accuracy desired).

Let us assume, then, that a satisfactory STO basis has been obtained. The corresponding one-electron basis can still be improved by introducing the notion of natural spin-orbitals.

2.2. The Reduced First Order Density Matrix

The reduced first order density matrix (1-matrix) enters our problem when we try to improve the basic spin-orbitals. It is defined as(16)

$$\gamma(x_1'|x_1) = N \int \Psi^*(x_1' x_2 \ldots x_N)\, \Psi(x_1 x_2 \ldots x_N)\, dx_2 dx_3 \ldots dx_N \ .$$

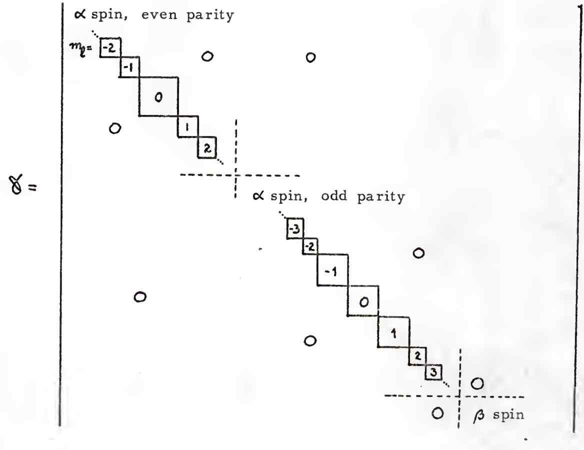
For a CI wave function $\Psi = \Sigma_i D_i c_i$, where the determinants D_i are made up of spin-orbitals ψ_k's,

$$\gamma(x_1'|x_1) = \sum_{kl} \left[\sum_{ij} (-1)^{P_{ij}} c_i^* c_j \right] \psi_k^*(x_1')\, \psi_l(x_1)$$

where the second sum goes over all the pairs (ij) of determinants D_i and D_j differing, at most, in the spin-orbitals k and l. This expression may be written as:

$$\gamma(x_1'|x_1) = \sum_{kl} \gamma_{kl} \, \psi_k^*(x_1') \, \psi_l(x_1) \quad .$$

The matrix $\boldsymbol{\gamma}$ of the γ_{kl}'s can be easily calculated. Since the generating function Ψ is an eigenfunction of $\mathbb{P}$, L_z and S_z, the operator $\gamma(1'|1)$ commutes with $\mathbb{P}(1)$, $L_z(1)$ and $S_z(1)$; this follows immediately from the properties of matrix elements between Slater determinants.(23) The matrix $\boldsymbol{\gamma}$ is then block-diagonal in the following manner:



The wave function Ψ is assumed to be an eigenfunction of L^2 and S^2. If, in addition, Ψ belongs to a state with $M_L = 0$, the block associated with m_ℓ is identical to the one with $-m_\ell$, for a given m_s and parity, because in this case, Ψ is invariant under space conjugation. Analogously, if Ψ belongs to a state with $M_S = 0$, the block with α spin is equal to the one with β spin. In connection with the selection of the one-electron basic set (see Sections 2.3 and 5.3), these properties can always be taken advantage of for the following reason: it can be proved$^{(23)}$ that the Hamiltonian matrix, in a basis of eigenfunctions to L^2 and S^2, is independent of M_L and M_S. This implies that, if the elements of degenerate spaces, for different M_L values, are related among themselves by

$$L_\pm \, \Phi_K^{(p)}(L, M_L) = [(L \mp M_L)(L \pm M_L + 1)]^{\frac{1}{2}} \, \Phi_K^{(p)}(L, M_L \pm 1) \qquad (2.1)$$

and an analogous relationship holds for the different M_S values, the coefficients a_{Kp} in Eq. (1.2) are the same, independently of M_L and M_S. In Eq. (2.1), the symbol $L_\pm$ stands for either the step-up or the step-down orbital angular momentum operator. Therefore, under the conditions above, the study of the convergence of the CI expansion for an L, S state can be performed without reference to the M_L and M_S values.

When Ψ belongs to a state with L = 0, the corresponding 1-matrix commutes with $L^2(1)$: then, the s and d orbitals do not mix, neither do the p's and f's, and all the blocks of a given ℓ-symmetry type are equal.

The 1-matrix can be diagonalized by a linear transformation. Its eigenvalues n_i are called occupation numbers. Its eigenfunctions χ_i are called natural spin-orbitals (NSO's) of the wave function from which γ is constructed. The 1-matrix becomes

$$\gamma(1'|1) = \sum_i n_i \chi_i^*(1') \chi_i(1)$$

2.3. Natural Radial Orbitals

In this section, we consider 1-matrices derived from Ψ 's with $M_L = 0$ and $M_S = 0$ (for N odd, it is not possible to have $M_S = 0$, but the considerations below can still be applied to different blocks).

As mentioned in Section 2.2, the blocks of γ of the same ℓ-symmetry type are equal among themselves, if Ψ belongs to an L=0 state. When this is not the case, γ has different blocks for different values of m_ℓ, and, hence, various sets of radial parts of NSO's spanning the space defined by the radial parts of the original spin-orbitals. The question is: should one use different radial functions to represent the different m_ℓ's of the basic spin-orbitals, or should one choose, perhaps by a maximum density criterion, one of the sets of NSO's, and use it for all values of m_ℓ?

For clarity, let us select a specific example: we consider the case of the p-type NSO's of a ^3P wave function for a two-electron atom. There are two sets of these: the R_{il}'s, corresponding to $m_\ell = \pm 1$, and the $\bar{R}_{il}$'s, corresponding to $m_\ell = 0$, where the subscript i labels the i^{th} natural spin-orbital for both sets. Let us form the orbitals:

$$p_i^1 = R_{il}\, Y_{11} \quad \text{and} \quad \bar{p}_i^0 = \bar{R}_{il}\, Y_{10},$$

and from them, a determinant $(\bar{p}_i^0 p_i^1 /)$, where the notation is such that (i) orbitals to the left of the bar are associated with α spin, those to the right, with β spin, and (ii) the orbitals are positioned in order of increasing i, and, within a value of the subscript i, according to increasing m_ℓ values. Let us now obtain the ^3P projection of the above determinant:

$$O_{1,1}^{L^2, S^2} (\bar{p}_i^0 p_i^1 /) = (\bar{p}_i^0 p_i^1 /) - (p_i^0 \bar{p}_i^1 /)$$

where it has been necessary to introduce the following functions:

$$p_i^0 = R_{il}\, Y_{10} \quad \text{and} \quad \bar{p}_i^1 = \bar{R}_{il}\, Y_{11}$$

in which the original $m_\ell = 0$ radial part is mixed with the $m_\ell = 1$ spherical harmonic, and vice versa. Therefore, unnecessary redundancies arise in the description of eigenfunctions to L^2 and S^2 when the true NSO's are employed. In this work, we have chosen, for each ℓ-value, the radial functions associated with the set with largest leading occupation number, and used it for all m_ℓ values. Following Bunge,(28) these one-electron functions shall be called natural radial orbitals (NRO's).

2.4. Natural Spin-Orbitals for Systems with more than Two Electrons

Löwdin has suggested (29) that the NSO expansions of many-electron Ψ 's might have optimum convergence properties with respect to (i) truncations of the one-electron basic set, and (ii) truncations of the CI expansion. Both of these properties have been proved to be rigorously true for two-electron systems.(30) Concerning the first point, (i), our experience and that of other authors (20) shows that a non-optimized basis may be drastically truncated by using NSO's, but that this is not so when one employs the spin-orbitals formed from an optimum set of STO's, as is the case in the present calculation. As for (ii), it holds practically true for the ground states of the Be and Ne atoms,(20, 31) which have ^1S symmetry, and we shall try to find a way of extending it to other symmetries as well.

Let us consider a variational wave function Φ, made up of the HF configuration and all double excitations of a pair of HF spin-orbitals ψ_k, ψ_l :

$$\Phi(1,2,\ldots,N) = \det\{\prod_{i=1}^{N}\psi_i(i)\} + \det\{[(\prod_{i=1}^{N}\psi_i)/\psi_k(k)\psi_l(l)]\sum_{\substack{p>N\\q>N}}\psi_p(k)\psi_q(l)c_{pq}\}$$

$$= \Phi_{HF} + \Phi^{(k,l)} \qquad (2.2)$$

where $\{\psi_i;\ i=1,\ldots,N\}$ spans the HF space, $\{\psi_p;\ p=N+1,\ldots,M\}$ defines an orthogonal complement to the HF space, and the c_{pq}'s are variational parameters. The corresponding 1-matrix, $\gamma(\Phi)$, has the same eigenfunctions and eigenvalues as the 1-matrix derived from $\varphi(1,2)$

$$\varphi(1,2) = \det\{\psi_k\psi_l\} + \det\{\sum_{\substack{p>N\\q>N}}\psi_p\psi_q c_{pq}\}$$

$$= \det\{\psi_k\psi_l\} + \chi^{(k,l)}$$

where the c_{pq}'s are those from Eq. (2.2). In addition, $\gamma(\Phi)$ has the eigenfunctions $\{\psi_i;\ i=1,\ldots,N; i\neq k; i\neq l\}$, each with eigenvalue equal to one. When $\varphi(1,2)$ is expressed in terms of its NSO's (let us call them (k,l) pair NSO's), $\chi^{(k,l)}$ is transformed into $\chi^{(k,l)}_{nat}$, which, according to the two-electron theory, has optimum convergence properties with respect to $\chi^{(k,l)}$.

Next, we shall consider a new variational wave function Φ

$$\Phi = \Phi_{HF} + \Phi^{(k,l)} + \Phi^{(m,n)}$$

where, for definiteness, $k < l < m < n \leq N$, and $\Phi^{(m,n)}$ is defined in a way entirely analogous as $\Phi^{(k,l)}$. Its NSO's shall be called *(k, l)(m, n) pair NSO's*. Under certain conditions, these may be subdivided in two sets: one of them, similar to the set of (k, l) pair NSO's; the other, similar to the set of (m, n) pair NSO's. This implies that the (k, l)(m, n) pair NSO's are nearly optimum for expanding both pairs of HF spin-orbitals, while still constituting an orthogonal set. It has been shown that such a property is very closely fulfilled for the ground state of Be,[(20)] for which the KL shell NSO's are obtained from the wave function

$$\Psi^{(KL)} = (1s)^2(2s)^2 + \det\{[\sum_{i \leq j} {}^1S(x_i x_j)k_{ij}](2s)^2\}$$

$$+ \det\{(1s)^2[\sum_{i \leq j} {}^1S(x_i x_j)l_{ij}\}$$

One can expect an analogous behaviour for the joint NSO's of any number of weakly interacting electron pairs.

Let us advance the hypothesis that the NSO expansions have optimum convergence properties, in general, for any *group* of electrons localized in the same region of space. If this is true, the joint NSO's of weakly interacting groups may also be subdivided in two sets, resembling those of the individual groups. For atoms in the first row of the periodic table, there are two distinct groups, corresponding to the K and L shells.

The alternatives for the choice of the basic one-electron functions are as follows:

a) K shell NSO's; optimum convergence in the K shell; poor convergence in the L shell.

b) L shell NSO's; poor convergence in the K shell; optimum convergence in the L shell.

c) KL shell NSO's; good convergence for both shells.

Since the triple and quadruple excitations appear largely as products of double and single (or double and double) excitations, a poor convergence in either shell means a poor convergence of these as well. As for the Intershell configurations, any basis which is good for them appears to be extremely bad everywhere else, and they shall hence not enter our discussion at this point.

In the next section, we shall describe the particular choice of NSO's used in the present calculation.

2.5. Final Set of One-Electron Functions

We have learned by experience that most of the difficulties lie in the L shell. Thus, in a first attempt, we concentrate our efforts in obtaining the best possible set of one-electron functions in which to expand the L shell, even if this has to be done at some expense of the K shell and of several triple and quadruple excitations. A KL shell NSO basis should be tried next.

Let us consider all the orbitals formed from the HF STO's and those which were optimized for the L shell. A CI expansion is then set up, which includes almost all of the L shell double excitations, and the corresponding L shell NSO's are obtained. (In order to preserve the HF spin-orbitals as NSO's, a few configurations are omitted: this is illustrated in Chapter V for the case of the ^3P state of the carbon atom.) It should be pointed out here that, except for ^1S states, one does not deal with NSO's but with NRO's, as explained in Section 2.3.

The L shell NRO's are optimum to expand the L shell; one can only hope that the convergence of the K shell and Intershell expansions in that basis is not too slow. In order to improve the effects of those configurations containing the remaining orbitals (i.e. those formed from STO's optimized in the K shell and Intershell), we obtain the tail NRO's: these are the NRO's of a CI wave function consisting solely of the HF configuration plus the K shell and Intershell configurations containing the "remaining orbitals" described above. The tail NRO's are automatically orthogonal to the L shell ones, since the two sets are made up of orbitals which are orthogonal among themselves.

CHAPTER III

CRITERIA FOR THE SELECTION OF CONFIGURATIONS

Three main criteria are commonly used in most CI calculations for selecting the configurations, and the choice of a criterion depends, to a large extent, on the particular use one wishes to make of the wave function, and also on the personal preferences of each author. In this work we have taken into account all three of them, at various stages of our calculation. Let us briefly describe them here.

3.1. Second Order Perturbation Theory

In the Rayleigh-Schrödinger (RS) perturbation theory, the second order correction to the energy is given by the formula:

$$E^{(2)} = \sum_i H_{oi}^2/(E_o - H_{ii})$$

where $H_{oi} = \langle \Phi_o | H | \Phi_i \rangle$, Φ_o is the wave function for the unperturbed Hamiltonian H_o

$$H_o \Phi_o = E_o \Phi_o \quad ,$$

and $\{\Phi_i\}$ defines a complete set of symmetry adapted functions spanning the orthogonal complement to Φ_o. If we choose $\Phi_o = \Phi_{HF}$ and $\{\Phi_i\} = \{\Phi_K^{(p)}\}$, the contribution of each term $\Phi_K^{(p)}$ to the second order energy is given by

$$E_{Kp}^{(2)} = \langle \Phi_{HF} | H | \Phi_K^{(p)} \rangle^2 / (E_{HF} - \langle \Phi_K^{(p)} | H | \Phi_K^{(p)} \rangle) \quad .$$

This expression has the advantage that one can calculate it *a priori*, and, hence, have an idea of the importance of the HF interacting terms of the CI expansion.

For ^1S states of two-electron systems, the RS perturbation expansion converges fast,$^{(32, 33)}$ and in addition, the $E_{Kp}^{(2)}$'s are reasonably good approximations to the energy contributions of the individual terms, as found by straight application of the variational method. Furthermore, their goodness improves with increasing nuclear charge Z.$^{(34)}$

However, for outer electron pair excitations, the RS expansion converges slowly:$^{(33)}$ $E^{(2)}$ is a poor energy correction, and the $E_{Kp}^{(2)}$'s are often not even of the correct order of magnitude.

The second order perturbation theory criterion is hence quite rough, and it can only be used in the very first stage of the calculation.

3.2. Eigenvector Components

Only within the expansion of a given pair of electrons, does the magnitude of the eigenvector component provide an energy criterion for selecting configurations: as pointed out in Reference 20, these magnitudes are larger for configurations which correlate outer electrons, than for those correlating electrons closer to the nucleus, when the energy contributions are the same.

However, if one is interested not only in a good energy, but also in a good wave function, terms with relatively large eigenvector components but small energy contributions should be preserved, since they might be important to account for properties other than the energy.

3.3. Partial Energies

Let $\mathbb{H}$ be the matrix representation of the Hamiltonian in an orthonormal set $\{\Phi_i ; i=0,1,\ldots\}$. The eigenvalue equation is

$$\mathbb{H}\,\mathbb{c} = E\,\mathbb{c} \tag{3.1}$$

If a unit row vector $u=\underline{\overline{1\;0\;0\;.\;.\;.\;0\;.\;.\;.}}$ is applied from the left to both terms of Eq. (3.1), one gets

$$E = \Sigma_i \langle \Phi_o | H | \Phi_i \rangle c_i / c_o = \Sigma_i \; E_i$$

The E_k's defined in this way are called partial energies of Φ_k with respect to Φ_o.(35) They represent the actual energy contribution of Φ_k if (sufficient condition), when Φ_k is excluded from $\{\Phi_i\}$ the new eigenvector components c_i' satisfy

$$\frac{c_i}{c_o} = \frac{c_i'}{c_o'} \qquad \text{for all } i \neq k . \qquad (3.2)$$

The proof is very simple. Let us consider two secular equations differing only in that, in one of them, Φ_k is missing. Then, we have

$$E(-\Phi_k) = \sum_{i \neq k} \langle \Phi_o | H | \Phi_i \rangle c_i'/c_o'$$

$$E = \sum_{i \neq k} \langle \Phi_o | H | \Phi_i \rangle c_i/c_o + \langle \Phi_o | H | \Phi_k \rangle c_k/c_o$$

$$E - E(-\Phi_k) = \langle \Phi_o | H | \Phi_k \rangle c_k/c_o = E_k$$

The fulfillment of Eq.(3.2) is directly related to the stability of Ψ with respect to the exclusion of the term Φ_k; this depends on the nature of Φ_k alone. The stability of ψ is particularly good when $\Phi_o = \Phi_{HF}$, or, even better, when $\Phi_o = \Phi_{TR}$, a normalized truncation of a CI wave function which includes the HF configuration; it is still further improved when the Φ_i's are constructed from NRO's.

3.4. Optimum Convergence

In our criterion for optimum convergence of a fixed size CI expansion, we shall take into consideration both the eigenvector component and the partial energy of each term.

It is possible to find a value of the modulus of the eigenvector component, EIG, below which the terms crowd together, most of them contributing very little to the energy; a few of these, however, do have sizable partial energies, and one can set a tolerance, TOL, such that the terms for which the absolute value of the partial energy exceeds TOL are separated from the rest.

In our 234-terms CI expansion for the C atom, we shall preserve all the terms with eigenvector component larger than EIG= 0.0035, and, out of the remaining ones, those having a partial energy (in absolute value) larger than TOL= 0.000012 a.u.

The convergence is arbitrarily said to be optimum, if no 234-terms CI wave function can be found, which gives the same (or a better) total energy for smaller EIG and TOL values.

CHAPTER IV

THE BASIC N-ELECTRON FUNCTIONS

As mentioned in Section 1.3, the basic N-electron functions are orthonormalized projected configurations, or terms, $\Phi_K^{(p)}$. We shall describe here how to form them. Except for the determination of degeneracies, which can easily be done by hand, the obtaining of the terms is implemented in a computer program (see Section 5.1).

4.1. Degeneracy of a Configuration

The degeneracy of a configuration K for the state under consideration determines the number of LS terms belonging to K. It is evaluated in the following manner: first, all equivalent spin-orbitals are combined according to the vector coupling model and the Pauli principle,(36) to form all the possible multiplets. Then, all the multiplets arising from all the groups of equivalent electrons are in turn coupled together, in any order; this gives a set of multiplets, some of them appearing several times; the number of times a given multiplet can be formed in this way, is the degeneracy g_K

of the configuration K, for that multiplet.

Let us illustrate this procedure with a specific example: the degeneracy of the configuration $(s_1)^2 s_2 s_3 (p_1)^2$ of the ^3P state of the carbon atom. The two equivalent spin-orbitals $(s_1)^2$ can only give a ^1S. Hence, the ^3P must be formed by coupling the remaining four spin-orbitals: $(p_1)^2$ gives a ^1D, a ^3P and a ^1S; $s_2 s_3$ gives a ^3S and a ^1S. The two possible couplings that yield a ^3P are:

$$^1S(s_1)^2 \; ^3P\{^3S(s_2s_3) \; ^3P(p_1)^2\} \quad \text{and} \quad ^1S(s_1)^2 \; ^1S(s_2s_3) \; ^3P(p_1)^2$$

Thus, the degeneracy is equal to two.

4.2. Projection of a Configuration

In the case of the orbital and spin angular momenta, the projection operator O_λ^Λ of Eq. (1.1) can be written in a more practical form,$^{(22)}$ in terms of the well-known step-up and step-down operators M_+ and M_-, defined by $M_+ = M_x + i M_y$ and $M_- = M_x - i M_y$:

$$O_{k,m}^{M^2, M_z} = (2k+1)\frac{(k+m)!}{(k-m)!} \sum_{\nu=0}^{k_{max}-k} (-1)^\nu \frac{M_-^{(k-m+\nu)} M_+^{(k-m+\nu)}}{\nu!\,(2k+\nu+1)!} \qquad (4.1)$$

where M stands for either L or S, k(k+1) is the eigenvalue of M^2 we wish to project, and m is the eigenvalue of M_z, which is assumed to be known. The only possible k-values range, at most, from $k = m, m+1, \ldots$ up to a certain k_{max}, which may be evaluated by the addition theorem of angular momenta and which depends on the particular configuration.

The operator $O^{L^2, S^2}_{L, S}$, defined by Eqs.(1.3) and (4.1), can be easily applied to any Slater determinant D_{Kp}:

$$\Phi'^{(p)}_K = O^{L^2, S^2}_{L, S} \; D_{Kp} = \sum_{\alpha=1}^{n_K} D_{K\alpha} \, d^{(p)}_{K\alpha} \qquad (4.2)$$

In Eq.(4.2), n_K is the number of determinants which span the space $\{K; L, S, M_L, M_S\}$; not all the $D_{K\alpha}$'s with the correct M_L and M_S values, belong to this space; also, some of the $d^{(p)}_{K\alpha}$'s may be equal to zero.

Let us assume that the configuration K is degenerate, and let us project another determinant D_{Kq}. If the corresponding projection $\Phi'^{(q)}_K$ is linearly independent of $\Phi'^{(p)}_K$, the two functions may be Schmidt orthogonalized; if not, one follows the same procedure with another determinant, and so on, until g_K independent $\Phi'^{(p)}_K$'s have been found. The orthonormalized functions are the $\Phi^{(p)}_K$'s of Eq.(1.4).

The obtaining of the independent $\Phi^{(p)}_K$'s is not quite as "trial and error" as might be deduced from the above description. In fact, one soon discovers many empirical rules, and, with a little practice, one guesses immediately which determinants to project.

4.3. Partition of Degenerate Spaces

The degenerate configurations would not create any special problems were it not for the fact that their degeneracies, in the case of atoms larger than Be, are often very large (for C, the largest degeneracy among subclasses giving rise to double excitations, is 27); the number of terms to be considered becomes extremely large, and a great many of them contribute enough to the energy so that they may not be ignored; as a result, the convergence of the CI expansion is exceedingly slow.

For the purpose of illustrating this problem and how it is solved here, let us consider the subclass $(s_x)^2(p_y)^2(d_z)^2$ of the carbon atom, which is 6-degenerate in the ^3P multiplet. We find six Slater determinants with $M_L = 1$ and $M_S = 1$, whose projections are linearly independent, and we obtain the corresponding $\Phi_K^{(p)}$'s. When these are introduced into the secular equation, we observe, in general, that the contribution of the configuration $(s_1)^2(p_1)^2(d_1)^2$ is very much spread over all of the terms. Since there are $6! = 720$ different ways of partitioning the 6-degenerate space, just by changing the sequence in which the projected determinants are successively orthogonalized, and furthermore, the set of six determinants is not unique, one speculates that some choice might be such that only one or two of the terms are important.

A given ordered and complete set of determinants to be projected for a given subclass determines a particular partition of the degenerate space of that subclass. We shall try to find an optimum partition.

According to the many-electron theory, (24) one expects that terms with vanishing Hamiltonian matrix elements with the HF configuration give negligible or small contributions both to the energy and to the wave function. It seems reasonable to try a partition in which the first five determinants to be projected are three- and four-excited determinants, and the sixth one is a two-excited one. In the case under consideration, for example, we could have:

$(s_1 p_1^1 d_1^{\bar{2}} d_1^2 / s_1 p_1^0)$	three excited
$(s_1 p_1^{\bar{1}} p_1^1 d_1^{\bar{1}} / s_1 d_1^2)$	three
$(s_1 p_1^{\bar{1}} d_1^0 d_1^1 / s_1 p_1^1)$	four
$(s_1 p_1^1 d_1^{\bar{1}} d_1^0 / s_1 p_1^1)$	three
$(s_1 p_1^0 d_1^{\bar{2}} d_1^2 / s_1 p_1^1)$	three
$(s_1 p_1^0 p_1^1 d_1^{\bar{2}} / s_1 d_1^2)$	two

It should be noted at this point, that it is not always possible to partition the degenerate space in this way: for some double excitations, it might be necessary to have more than one two-excited determinant, in order to span the full degenerate space.

Obviously, the partial energy contributions for the first five projections (which are projections of linear combinations of the first five determinants) are zero since

$$\langle \Phi_{HF} | H | \Phi_K^{(p)} \rangle = 0 \quad ; \; p = 1, 2, 3, 4, 5.$$

Now, the interaction of a configuration with the HF configuration is a constant given by:

$$\frac{1}{a_{HF}} \langle \Phi_{HF} | H | [\Sigma_p \, \Phi_K^{(p)} a_{Kp}] \rangle = \sum_{p=1}^{g_K} E_{Kp}$$

where a_{HF} is the coefficient of the HF configuration, and the a_{Kp}'s are those of the $\Phi_K^{(p)}$ terms of configuration K in the final wave function. This implies that $\Phi_K^{(6)}$ must have maximum interaction with the HF configuration, provided that, under any other partitions, the E_{Kp}'s be always negative or zero, which is the case for most configurations. Of course, the partial energies with respect to Φ_{TR} (see Section 3.3), will not be necessarily zero for the first five terms: in the example shown above, we have only succeeded in finding an appropriate partition in which all the two-body correlations (two-excited determinants) are lumped together into the last element of the degenerate configuration.

CHAPTER V

CALCULATION

5.1. The Computer Program

Our CI calculation of the ground state of the carbon atom is performed with a computer program originally written by Bunge,(20) and later improved with the addition of a projection operator section and modified for use with highly degenerate configurations. Let us summarize briefly the main parts of the program in its present form.

There is first a very simple input, which specifies the type of work requested (CI + configuration search; optimization of STO parameters; CI + corresponding γ and NRO's; ..., etc.), the number of electrons N , the maximum size of the secular equation during search, the LS state, the STO parameters and coefficients, the determinants to be projected, the configurations and their degeneracies, and finally, the terms to be inserted in the CI expansion. Unless previously calculated and stored on magnetic tape, the one- and two-electron integrals are evaluated in double precision arithmetic. The next step is to generate and/or read the "Master Tape", which contains all the relevant information about the subclasses, their b and c coefficients and corresponding Slater determinants, and all the configurations considered. To each term the program associates a number, which is all one needs to specify in the input when such term is wanted in the CI expansion. Any selection of terms is permissible. The Hamiltonian matrix is computed as described in Section 1.3, and diagonalized by the Givens method.(37) Finally, if desired, the 1-matrix is calculated and the NRO's are obtained. If instead, one wishes to search for the most important terms out of a large number of them, the program can discard certain terms, according to the tolerance in the eigenvector components and the partial energies indicated in the input, pick up new terms, obtain the corresponding E and Ψ, discard some terms again, . . . , and so on until all the terms have been tried.

The last part of our calculation was performed on a CDC 3600/3400 electronic computer, with 41 K available words. The program, as adapted to this machine, permits a maximum size of the secular equation of 234x234, a maximum degeneracy of 27, and no more than 400 Slater determinants in the expansion of the projection of a given determinant. In addition, for each configuration, the number of terms inserted times the size of the secular equation, may not exceed 4000. The lowest eigenvalue and its corresponding eigenvector can be found in less than seven minutes, while the generation of the Hamiltonian matrix takes between three and forty minutes, depending on the configurations involved.

5.2. The STO Basis

We use as a starting point, the nominal HF wave function calculated by Bagus, (25) with an STO basis consisting of four s- and three p-type STO's, denoted as follows:

$$\text{for } \ell = 0\,, \quad S_{j0} \quad \text{with } j = 1, 2, 3, \text{ and } 4\,,$$
$$\text{for } \ell = 1\,, \quad S_{j1} \quad \text{with } j = 1, 2, \text{ and } 3.$$

In addition to the three HF orbitals s_1, s_2, p_1, four more orbitals can be formed from such a basis, i.e. s_3, s_4, p_2, and p_3. We arbitrarily postulate an s_3 consisting only of S_{30}, and orthogonalize it to the HF orbitals: s_3 becomes a linear combination of all four S_{j0}'s. The remaining orbitals are similarly obtained.

Some preliminary L shell NRO's are then constructed from the (4s, 3p) orbital basis, in the way outlined in Section 2.5, thereby removing the arbitrariness in the orthogonalizations above (the L shell NRO's are uniquely defined, since they are derived from a wave function which is invariant under linear transformations of the symmetry spin-orbitals other than the HF ones). A full L shell CI calculation with respect to single and double excitations is carried out with these "preliminary" L shell NRO's, and a selection, L(4, 3, 0, 0), is made of the most important terms; the letter L indicates that the terms are L shell excitations, and the ciphers inside the parentheses denote, in order, the number of s, p, d, and f orbitals involved.

Let us now energy optimize a d-type orbital, d_1, consisting of a single STO, S_{12}, using an expansion which includes L(4, 3, 0, 0) plus all the L shell single and double excitations that can be formed with d_1. Next, the expansion L(4, 3, 1, 0) is used as a starting point to optimize S_{13}, and in a similar way, the process is applied successively to S_{41}, S_{50}, S_{22}, and S_{23}. Any further attempts to extend the L shell STO basis, give negligible improvements in the energy: the "saturation" remainders are about 0.00010 a.u. for s-type STO's, 0.00010 a.u., 0.00017 a.u., and 0.00010 a.u. for p- d-, and f-type STO's respectively.

It is interesting to note that, often, more than one absolute minimum can be obtained for E, as a function of the STO parameters. Let us denote the latter by $(n_j ; Z_{j\ell})$, and let us consider the optimization of S_{41}. We find three sets (1 ; 1.3), (1 ; 2.3), and (2 ; 2.4) located in slightly different regions along the r axis, yet giving the same energy minimum. We choose (2 ; 2.4) because it is more orthogonal to the other S_{j1} functions, and therefore one can expect a greater flexibility in the CI expansion.

The final L shell NRO's are now evaluated as described in the next section: from here on, the symbols $s_1, \ldots, s_5, p_1, \ldots, p_4, d_1$, and

d_2 denote L shell NRO's. The subscripts are used to classify the NRO's according to decreasing occupation numbers of the 1-matrix block from which they are selected. The f-type NRO's need not be obtained because very few terms containing f_1 and f_2 appear in the CI expansion.

Next, let us consider the Intershell expansion ($s_1 s_2$ and $s_1 p_1$ excitations). Two parallel CI calculations are performed, one involving Intershell excitations alone, I(5, 4, 2, 2), and one on both L shell and Intershell excitations, LI(5, 4, 2, 2). A comparison of the partial energies of the Intershell terms in both CI wave functions, shows no appreciable differences, and hence, I(5, 4, 2, 2) is used as a starting point for the optimizations of $S_{60}^{(I)}$, and $S_{51}^{(I)}$ (the necessity for the superscript I, meaning Intershell, will be apparent below).

Independently, we consider the K shell. A comparison of the partial energies of the K shell terms in K(5, 4, 2, 2) and KL(5, 4, 2, 2), justifies our using K(5, 4, 2, 2) for the optimizations of $S_{60}^{(K)}$, $S_{70}^{(K)}$, $S_{51}^{(K)}$, $S_{61}^{(K)}$, $S_{32}^{(K)}$, $S_{42}^{(K)}$, and $S_{33}^{(K)}$. Once $S_{60}^{(K)}$, $S_{51}^{(K)}$, and $S_{61}^{(K)}$ have been found, the K shell NRO's are obtained: in this entirely new orbital basis, K(6, 6, 2, 2) converges very fast, which simplifies enormously the search for the remaining $S_{j\ell}^{(K)}$'s. The K shell NRO's, however, are no good for expanding the L shell, and hence they will not be used any further.

When $S_{60}^{(K)}$, $S_{70}^{(K)}$, $S_{51}^{(K)}$, and $S_{61}^{(K)}$ are used in an Intershell

CI, the results are even better than those obtained with $S_{60}^{(I)}$ and $S_{51}^{(I)}$. These STO's are hence abandoned in favor of their K shell counterparts, and the superscripts are dropped. Also, no $S_{j2}^{(I)}$ or $S_{j3}^{(I)}$ are considered, assuming that their K shell counterparts do an equally good job.

The overall "saturation" remainders for the Intershell are probably smaller than 0.00020 a.u. For the K shell, they can be estimated very accurately, from the C^{4+} spdf energy limits,(34) and the computation of the exclusion effects (see Chapter VI).

The simultaneous optimization of two STO's is found to be useful only in the case of S_{12} and S_{22}, where the net gain over the corresponding successive optimization is 0.000050 a.u.

The STO parameters are given in Table 1.

5.3. The NRO Basis

In order to obtain a set of L shell NRO's among which the three HF orbitals appear unchanged, we select a CI expansion containing the HF configuration and the L shell terms, but from which certain subclasses and configurations have been banished. There must be no two configurations differing in only one orbital, where the latter is either one of the HF orbitals. For example, the configuration $(s_1)^2 s_2 s_x (p_1)^2$ interacts with the HF configuration $(s_1)^2(s_2)^2(p_1)^2$ to produce a mixing of s_2 with s_x, i.e. the second s-type NRO is a linear combination of s_2 and s_x; also, $(s_1)^2(p_1)^3 p_2$

TABLE 1

STO BASIS

j	$n\ell$[a]	$Z_{j\ell}$	Shell[b]
1	1s	9.153	K (HF)
2	1s	5.382	K (HF)
3	3s	3.076	L (HF)
4	2s	1.428	L (HF)
5	3s	2.200	L
6	2s	10.500	K
7	3s	12.000	K
1	2p	5.152	L (HF)
2	2p	2.177	L (HF)
3	2p	1.150	L (HF)
4	3p	2.300	L
5	2p	9.000	K
6	3p	11.000	K
1	3d	1.950	L
2	4d	2.000	L
3	3d	11.800	K
4	4d	13.000	K
1	4f	2.500	L
2	5f	4.100	L
3	4f	16.000	K

---

a. The usual $(n\ell)$ notation is employed; where $n = n_j + \ell + 1$.

b. Localized mainly in the shell indicated.

interacts with $(s_1)^2(p_1)^4$ to mix p_1 and p_2.

In addition, as pointed out in Section 2.2, there shall be a mixing of s- and d-type orbitals, and of p- and f-type orbitals, unless the state under consideration has L= 0. This is due to interactions between configurations such as $(s_1)^2 s_x d_y (p_1)^2$ and $(s_1)^2(s_x)^2(p_1)^2$; however, the most important term of $(s_1)^2 s_x d_y (p_1)^2$ can be written as a linear combination of determinants which are two-excited with respect to $(s_1)^2(s_x)^2(p_1)^2$: the s_x-d_y mixing could be avoided, were it not for the presence of $(s_1)^2(d_y)^2(p_1)^2$ and $(s_1)^2 d_y d_z (p_1)^2$. Although some of the configurations of the type $(s_1)^2 s_x d_y (p_1)^2$ are extremely important, we prefer to obtain the NRO's which optimize the convergence of the CI expansion with respect to the highly degenerate $(s_1)^2(d_y)^2(p_1)^2$ and $(s_1)^2 d_y d_z (p_1)^2$.

For the calculation of the matrix γ, it is convenient, as explained in Sections 2.2 and 2.3, to use projected configurations corresponding to $M_L = 0$ and $M_S = 0$. Of course, this involves a great deal of additional work, inasmuch as one has to select a whole new set of projected determinants for each subclass. However, γ is greatly simplified, since only the block with α spin needs to be calculated, and within it, for each parity, only those blocks with different m_ℓ values. In our case, since we have used only s, p, and d orbitals in the calculation of γ, there are six different blocks instead of eighteen. The main advantage of this manner of proceeding, is that it makes a given choice of NRO's optimum for a larger number of spin-orbitals; for example, for the d-type orbitals, there are three different blocks corresponding to $|m_s|=\frac{1}{2}$ and $|m_\ell|=0, 1$, and 2, and hence three(instead of ten) different sets of radial parts of NSO's from which to select the set with largest leading occupation number. For the p-type NRO's, the $|m_\ell|=1$ block is used; for the d-type ones, the $|m_\ell|=2$ block.

The tail NRO's of the K shell are obtained by using a "tail" CI expansion, consisting solely of the HF configuration and all the K shell configurations formed from the following basic orbitals: s_1, $s_2, s_6, s_7, p_1, p_5, p_6, d_3$, and d_4, with the exception of the HF mixing and the s-d mixing configurations. Of course, the energy of such a CI wave function is expected to be quite bad. The advantage in obtaining the tail NRO's is, that the convergence of the final CI expansion is improved with respect to these orbitals, when the proportion in which the tail configurations enter the final CI wave function is the same as in the tail CI. For instance, let us consider the K shell excitations $(d_3)^2$, $(d_4)^2$, and d_3d_4: the only relevant terms are those for which the K shell remains coupled to ^1S symmetry, and thus the analogy with two-electron systems is valid, i.e. the contribution of d_3d_4 in terms of tail NRO's vanishes identically, while that of $(d_3)^2$ is increased. The tail NRO's would probably be more interesting if s_4, s_5, and p_4 were allowed to participate in the tail CI expansion.

The STO coefficients of the final basis are given in Table 2.

TABLE 2

ORBITAL EXPANSION COEFFICIENTS IN TERMS OF STO BASIS

s-type orbitals

j	s_1	s_2	s_3	s_4	s_5	s_6	s_7
1	0.08367000	- 0.00603915	- 0.09369030	- 0.07760310	2.96255656	2.98672805	8.84644190
2	0.92300001	- 0.22225095	- 0.12744686	0.63111113	- 3.20788800	- 9.32806898	- 7.24706571
3	0.00373000	0.28311059	1.98442364	- 2.06909513	2.16890838	3.52079834	1.94158740
4	-0.00049000	0.77062150	- 2.11510743	- 6.73457807	3.04802002	4.00795678	1.81114419
5	0.	0.	0.29320122	8.53761869	- 4.60005918	- 6.38148640	- 3.05801164
6	0.	0.	0.	0.	0.	1.90094936	-13.81750782
7	0.	0.	0.	0.	0.	4.16730904	12.85534277

p-type orbitals

j	p_1	p_2	p_3	p_4	p_5	p_6
1	0.02471983	0.00875016	- 0.23904545	2.57909541	- 5.08062824	- 5.71210320
2	0.39515727	1.34947380	3.51433573	- 6.61723276	7.96699593	7.46873578
3	0.64974551	- 1.58860309	2.22521976	- 1.52922492	1.36957226	1.08703423
4	0.	0.30004515	- 5.42984466	6.57390294	- 7.12843717	- 6.34128083
5	0.	0.	0.	0.	2.81890944	- 4.54819456
6	0.	0.	0.	0.	0.00193641	7.78219989

	d-type orbitals				f-type orbitals		
j	d_1	d_2	d_3	d_4	f_1	f_2	f_3
1	0.91478654	- 2.96733568	- 0.65621535	- 0.63157347	1.00000000	- 2.03480727	0.08838101
2	0.08956925	3.10385129	0.59309515	0.56296312	0.	2.26725398	- 0.13495018
3	0.	0.	0.48692690	- 4.34570943	0.	0.	1.00230449
4	0.	0.	0.54258688	4.38247015			

5.4. The Terms

Let us consider the very important 3-degenerate configuration $(s_1)^2 s_2 (p_1)^2 d_1$. The complete determinantal space of this configuration, for $M_L = 1$ and $M_S = 1$, is made up of 14 determinants; it involves both one-, two-, and three-excited determinants. As explained in Section 4.3, one looks for sets of three linearly independent projected determinants, containing as many three-excited ones as possible: in this case, only one. We chose the set:

$(s_1 s_2 p_1^{\bar{1}} d_1^2 / s_1 p_1^0)$	three excited
$(s_1 s_2 p_1^0 p_1^1 / s_1 d_1^0)$	one
$(s_1 p_1^{\bar{1}} p_1^1 d_1^1 / s_1 s_2)$	two

No special reason will be given for this choice; it can only be based on trial and error, and it would take too long to find the optimum set, out of all the possible ones having a three-excited determinant as their first component.

The advantages of the procedure outlined in Section 4.3 for partitioning the degenerate space, become much more obvious when one considers configurations such as $s_1 s_2 (p_1)^2 p_2 p_3$, which is 27-degenerate. It is possible, in this case, to find 25 linearly independent projections of three- and four-excited determinants. The 26th and 27th components of the set are projections of two-excited determinants, and they are found to correspond to the couplings

$^1S\,\{^3S(s_1s_2)\,^3S(p_2p_3)\}\,^3P(p_1)^2$ and $^1S(s_1s_2)\,^1S(p_2p_3)\,^3P(p_1)^2$ respectively.

For most configurations involving K shell excitations $(xy)(s_2)^2(p_1)^2$, the terms have been chosen so that only one element makes any contribution to the energy: it invariably represents a coupling $^1S(xy)\,^1S(s_2)^2\,^3P(p_1)^2$, reflecting the strong tendency of the K shell to maintain the ^1S symmetry. Some core polarization is effected by configurations of the type $s_x(s_2)^2(p_1)^2d_y$ and $(s_2)^2(p_1)^2p_xf_y$, since the pairs (s_xd_y) and (p_xf_y) cannot be coupled to a ^1S.

For L shell configurations, the contributions of three- and four-excited determinants associated with double excitations are not negligible. For those subclasses, when we use the same partition of the degenerate space for both shells, we find that, although the term with coupling $^1S(s_1)^2\,^1S(xy)\,^3P(p_1)^2$ contributes the largest partial energy, all the other terms are often non-negligible too. It is necessary then, to look for an additional optimum partition within the remainder of the degenerate space: this is done, mainly, by changing the order in which the three- and four- excited determinants are projected; occasionally, different sets of projected determinants are tried. In general, all one achieves is to increase the partial energy contribution of the largest terms at the expense of the smaller ones. For configurations which are not very important, this is often enough to permit us to discard most of the terms.

The $(p_1)^2$ excitations are all non-degenerate, and so the coupling ${}^1S(s_1)^2\ {}^1S(s_2)^2\ {}^3P(xy)$ is the only possible one.

For single excitations such as $(s_1)^2 s_2 s_3 (p_1)^2$, the dominant term does not belong to the coupling ${}^1S(s_1)^2\ {}^1S(s_2 s_3)\ {}^3P(p_1)^2$ but, rather, to ${}^1S(s_1)^2\ {}^3P\{{}^3S(s_2 s_3)\ {}^3P(p_1)^2\}$. This can be explained in the following way: the first coupling involves only one-excited determinants, while the second one involves both one- and two-excited ones, the latter causing greater interaction with the HF configuration.

The terms of the subclasses appearing in the final CI expansion are given in Tables 3, 4, and 5. The subclasses are characterized by letter subscripts; the determinants are given for the simplest configuration of each subclass, rather than in general, because it seems easier to read them that way; they are written in the notation introduced in Section 2.3, and they are listed in the order in which they are projected. Since the projection coefficients $b_{K\alpha}^{(p)}$ are the result of a series of projections and orthonormalizations, it is not always possible to write them in the form of quotients of simple integers or radicals; in such cases, they are given in decimal form, the number of figures depending on the accuracy; when all the coefficients of the projection have the same denominator, the latter is written only once, for the first determinant.

The first ten subclasses of Table 3 are common to the K

TABLE 3

SLATER DETERMINANTS AND $b^{(p)}_{K\alpha}$ COEFFICIENTS OF L AND K SHELL CONFIGURATIONS

Subclass L1= K1 : $(s_w)^2 (s_x)^2 (p)^2$, 1 determinant, degeneracy= 1.

i	Determinants	$b^{(1)}_{K\alpha}$
1	$(s_1 s_2 p_1^0 p_1^1 / s_1 s_2)$	1

Subclass L2= K2 : $(s_w)^2 s_x s_y (p)^2$, 4 determinants, degeneracy= 2.

i	Determinants	$b^{(1)}_{K\alpha}$	$b^{(2)}_{K\alpha}$
1	$(s_1 s_2 s_3 p_1^0 / s_1 p_1^1)$	2	$2/\sqrt{2}$
2	$(s_1 s_2 p_1^0 p_1^1 / s_1 s_3)$		2

Subclass L3= K3 : $(s)^2 (p)^4$, 1 determinant, degeneracy= 1.

i	Determinants	$b^{(1)}_{K\alpha}$
1	$(s_1 p_1^{\bar{1}} p_1^0 p_1^1 / s_1 p_1^1)$	1

Subclass L4= K4 : $(s)^2 (p_w)^3 p_x$, 7 determinants, degeneracy= 3.

i	Determinants	$b^{(1)}_{K\alpha}$	$b^{(2)}_{K\alpha}$	$b^{(3)}_{K\alpha}$
1	$(s_1 p_1^{\bar{1}} p_1^1 p_2^0 / s_1 p_1^1)$	$5/\sqrt{10}$	$3/\sqrt{2}$	-1
2	$(s_1 p_1^{\bar{1}} p_1^0 p_2^1 / s_1 p_1^1)$		4	-2
3	$(s_1 p_1^0 p_1^1 p_2^0 / s_1 p_1^0)$			2

TABLE 3 continued

Subclass L5= K5: $(s)^2(p_w)^2(p_x)^2$, 12 determinants, degeneracy = 5.

i	Determinants	$b_{K\alpha}^{(3)}$	$b_{K\alpha}^{(4)}$	$b_{K\alpha}^{(5)}$
1	$(s_1p_1^{\bar{1}}p_1^1p_2^1/s_1p_2^0)$	0	$10/\sqrt{33}$	$2/\sqrt{3}$
2	$(s_1p_1^0p_2^0p_2^1/s_1p_1^0)$	$-1/\sqrt{2}$	0	0
3	$(s_1p_1^1p_2^{\bar{1}}p_2^0/s_1p_1^1)$	2	11	1
4	$(s_1p_1^0p_2^{\bar{1}}p_2^1/s_1p_1^1)$		22	2
5	$(s_1p_1^0p_1^1p_2^0/s_1p_2^0)$			3

Subclass L6= K6: $(s)^2(p_w)^2p_xp_y$, 28 determinants, degeneracy= 9.

i	Determinants	$b_{K\alpha}^{(8)}$
1	$(s_1p_1^0p_2^{\bar{1}}p_3^1/s_1p_1^1)$	$-6/\sqrt{24}$
2	$(s_1p_1^{\bar{1}}p_1^1p_3^1/s_1p_2^0)$	-10
3	$(s_1p_1^{\bar{1}}p_1^1p_3^0/s_1p_2^1)$	-10
4	$(s_1p_1^0p_2^1p_3^{\bar{1}}/s_1p_1^1)$	- 6
5	$(s_1p_1^1p_2^{\bar{1}}p_3^0/s_1p_1^1)$	- 3
6	$(s_1p_1^1p_2^0p_3^{\bar{1}}/s_1p_1^1)$	- 3
7	$(s_1p_1^{\bar{1}}p_1^0p_2^1/s_1p_3^1)$	- 5
8	$(s_1p_1^0p_1^1p_2^0/s_1p_3^0)$	12

The full degenerate space is obtained by projecting, in addition, the following determinant: $(s_1p_1^0p_2^0p_3^1/s_1p_1^0)$

TABLE 3 continued

Subclass L7= K7 : $(s_x)^2(p_y)^2(d_z)^2$, 27 determinants, degeneracy= 6.

i	Determinants	$b_{K\alpha}^{(2)}$	$b_{K\alpha}^{(3)}$	$b_{K\alpha}^{(4)}$	$b_{K\alpha}^{(5)}$	$b_{K\alpha}^{(6)}$
1	$(s_1 p_1^{1} d_1^{\bar{2}} d_1^{2}/s_1 p_1^{0})$	0.781508148	0.361963863	-2.923333333	1.801963268	$-5/\sqrt{45}$
2	$(s_1 p_1^{\bar{1}} p_1^{1} d_1^{\bar{1}}/s_1 d_1^{2})$	2.526215823	-0.518629654	-0.776059887	-0.724407157	$\sqrt{50}$
3	$(s_1 p_1^{\bar{1}} d_1^{0} d_1^{1}/s_1 p_1^{1})$		1.930314651	-1.112537987	-0.190117275	0
4	$(s_1 p_1^{1} d_1^{\bar{1}} d_1^{0}/s_1 p_1^{1})$			2.750684472	-2.946817765	0
5	$(s_1 p_1^{0} d_1^{\bar{2}} d_1^{2}/s_1 p_1^{1})$				3.796013990	5
6	$(s_1 p_1^{0} p_1^{1} d_1^{\bar{2}}/s_1 d_1^{2})$					15

Subclass L8=K8 : $(s)^2(p)^2 d_x d_y$, 58 determinants, degeneracy = 10.

i	Determinants	$b_{K\alpha}^{(5)}$	$b_{K\alpha}^{(8)}$	$b_{K\alpha}^{(10)}$
1	$(s_1 p_1^{\bar{1}} d_1^{1} d_2^{2}/s_1 p_1^{\bar{1}})$	0.2086440	-3.6547708	$\sqrt{15}/\sqrt{12}$
2	$(s_1 p_1^{1} d_1^{\bar{2}} d_2^{1}/s_1 p_1^{1})$	-1.0432202	3.5540488	$\sqrt{60}$
3	$(s_1 p_1^{0} d_1^{0} d_2^{1}/s_1 p_1^{0})$	0.	5.2163146	0
4	$(s_1 p_1^{\bar{1}} p_1^{0} d_2^{0}/s_1 d_1^{2})$	-0.4818428	-2.8909798	$-\sqrt{80}$
5	$(s_1 p_1^{1} d_1^{0} d_2^{0}/s_1 p_1^{0})$	3.5408069	-0.1220935	$\sqrt{120}$
6	$(s_1 p_1^{\bar{1}} p_1^{1} d_2^{\bar{1}}/s_1 d_1^{2})$		-2.1295515	$-\sqrt{60}$
7	$(s_1 p_1^{\bar{1}} d_1^{2} d_2^{\bar{1}}/s_1 p_1^{1})$		-1.1654978	$\sqrt{15}$

TABLE 3 continued

Subclass L8= K8 (continued).

i	Determinants	$b_{K\alpha}^{(5)}$	$b_{K\alpha}^{(8)}$	$b_{K\alpha}^{(10)}$
8	$(s_1 p_1^{\bar{1}} d_1^0 d_2^1 / s_1 p_1^1)$		6.1679395	$\sqrt{90}/\sqrt{12}$
9	$(s_1 p_1^0 d_1^{\bar{1}} d_2^2 / s_1 p_1^0)$			$-\sqrt{240}$
10	$(s_1 p_1^0 p_1^1 d_1^1 / s_1 d_2^{\bar{1}})$			$\sqrt{120}$

Subclass L9= K9: $(s)^2 (p)^2 (f)^2$, 42 determinants, degeneracy= 6.

i	Determinants	$b_{K\alpha}^{(3)}$	$b_{K\alpha}^{(5)}$	$b_{K\alpha}^{(6)}$
1	$(s_1 p_1^{\bar{1}} f_1^{\bar{1}} f_1^3 / s_1 p_1^0)$	$\sqrt{28}/\sqrt{15}$	0.	0
2	$(s_1 p_1^0 f_1^{\bar{1}} f_1^2 / s_1 p_1^0)$	$\sqrt{21}$	0.	0
3	$(s_1 p_1^1 f_1^{\bar{3}} f_1^2 / s_1 p_1^1)$	$\sqrt{140}$	0.	0
4	$(s_1 p_1^{\bar{1}} p_1^1 f_1^1 / s_1 f_1^0)$		-1.4819172	0
5	$(s_1 p_1^{\bar{1}} p_1^0 f_1^2 / s_1 f_1^0)$		2.8166174	$\sqrt{14}/\sqrt{15}$
6	$(s_1 p_1^0 p_1^1 f_1^0 / s_1 f_1^0)$			$\sqrt{105}$

Subclass L10= K10: $(s_w)^2 s_x (p)^2 d$, 14 determinants, degeneracy= 3.

i	Determinants	$b_{K\alpha}^{(2)}$	$b_{K\alpha}^{(3)}$
1	$(s_1 s_2 p_1^{\bar{1}} d_1^2 / s_1 p_1^0)$	$-\sqrt{3}/\sqrt{3}$	$-\sqrt{15}/\sqrt{3}$
2	$(s_1 s_2 p_1^0 p_1^1 / s_1 d_1^0)$	$\sqrt{50}$	$\sqrt{40}$
3	$(s_1 p_1^{\bar{1}} p_1^1 d_1^1 / s_1 s_2)$		$\sqrt{30}$

TABLE 3 continued

Subclass L11 : $(s_u)^2 s_w s_x p_y p_z$, 8 determinants, degeneracy = 3.

i	Determinants	$b^{(2)}_{K\alpha}$	$b^{(3)}_{K\alpha}$
1	$(s_1 s_2 s_3 p^0_2 / s_1 p^1_1)$	$1/\sqrt{3}$	1
2	$(s_1 s_3 p^1_1 p^0_2 / s_1 s_2)$	3	1
3	$(s_1 s_2 s_3 p^0_1 / s_1 p^1_2)$		2

Subclass L12 : $(s_w)^2 s_x p_y p_z d$, 32 determinants, degeneracy = 6.

i	Determinants	$b^{(2)}_{K\alpha}$	$b^{(4)}_{K\alpha}$
1	$(s_1 s_2 p^{\bar{1}}_1 d^2_1 / s_1 p^0_2)$	$-\sqrt{5}/\sqrt{12}$	$\sqrt{845}/\sqrt{396}$
2	$(s_1 p^{\bar{1}}_1 p^1_2 d^1_1 / s_1 s_2)$	$\sqrt{90}$	$-\sqrt{1690}$
3	$(s_1 s_2 p^{\bar{1}}_2 d^1_1 / s_1 p^1_1)$		$-\sqrt{640}$
4	$(s_1 s_2 p^{\bar{1}}_1 p^1_2 / s_1 d^1_1)$		$\sqrt{4840}$

i	Determinants	$b^{(5)}_{K\alpha}$	$b^{(6)}_{K\alpha}$
1		$\sqrt{5}/6$	$\sqrt{5}/\sqrt{12}$
2		$-\sqrt{10}$	$-\sqrt{90}$
3		$-\sqrt{40}$	$-\sqrt{40}$
4		$\sqrt{1000}$	$\sqrt{160}$
5	$(s_1 s_2 p^0_1 p^1_2 / s_1 d^0_1)$	$\sqrt{1080}$	$\sqrt{120}$
6	$(s_1 p^1_1 p^1_2 d^{\bar{1}}_1 / s_1 s_2)$		$\sqrt{160}$

TABLE 3 continued

Subclass L13: $(s_w)^2 s_x pdf$, 56 determinants, degeneracy= 6.

i	Determinants	$b_{K\alpha}^{(3)}$	$b_{K\alpha}^{(4)}$	$b_{K\alpha}^{(5)}$	$b_{K\alpha}^{(6)}$
1	$(s_1 s_2 p_1^{\bar{1}} f_1^3 / s_1 d_1^{\bar{1}})$	1.059148182	$\sqrt{175}/6$	$\sqrt{7}/\sqrt{18}$	$\sqrt{21}/\sqrt{18}$
2	$(s_1 s_2 d_1^{\bar{2}} f_1^3 / s_1 p_1^0)$	0.599144689	$\sqrt{14}/3$	$\sqrt{7}/3$	$\sqrt{42}$
3	$(s_1 p_1^{\bar{1}} d_1^1 f_1^1 / s_1 s_2)$	3.555121506	$\sqrt{2625}/18$	$\sqrt{35}/\sqrt{54}$	$\sqrt{35}$
4	$(s_1 s_2 p_1^{\bar{1}} d_1^2 / s_1 f_1^0)$		$\sqrt{560}/3$	$\sqrt{280}/3$	$\sqrt{420}$
5	$(s_1 s_2 p_1^0 d_1^0 / s_1 f_1^1)$			$\sqrt{70}/2$	$\sqrt{105}$
6	$(s_1 s_2 p_1^1 f_1^0 / s_1 d_1^0)$				$\sqrt{280}$

Subclass L14: $(s_w)^2 (s_x)^2 p_y p_z$, 2 determinants, degeneracy= 1.

i	Determinants	$b_{K\alpha}^{(1)}$
1	$(s_1 s_2 p_1^0 p_2^1 / s_1 s_2)$	2

Subclass L15: $(s_w)^2 (s_x)^2 (d)^2$, 2 determinants, degeneracy= 1.

i	Determinants	$b_{K\alpha}^{(1)}$
1	$(s_1 s_2 d_1^0 d_1^1 / s_1 s_2)$	$5/\sqrt{15}$

TABLE 3 continued

Subclass L16: $(s_w)^2(s_x)^2(f)^2$, 3 determinants, degeneracy= 1.

i	Determinants	$b^{(1)}_{K\alpha}$
1	$(s_1 s_2 f_1^0 f_1^1 / s_1 s_2)$	$7/\sqrt{21}$

Subclass L17: $(s)^2(p)^3 f$, 9 determinants, degeneracy= 1.

i	Determinants	$b^{(1)}_{K\alpha}$
1	$(s_1 p_1^{\bar{1}} p_1^0 f_1^1 / s_1 p_1^1)$	$\sqrt{35}$

Subclass L18: $(s)^2(p_w)^2 p_x f$, 44 determinants, degeneracy= 4.

i	Determinants	$b^{(1)}_{K\alpha}$
1	$(s_1 p_1^0 p_2^0 f_1^1 / s_1 p_1^0)$	$35/\sqrt{105}$

The full degenerate space is obtained by projecting, in addition, the following determinants: $(s_1 p_1^{\bar{1}} p_1^1 f_1^2 / s_1 p_2^{\bar{1}})$, $(s_1 p_1^{\bar{1}} p_2^0 f_1^3 / s_1 p_1^{\bar{1}})$, $(s_1 p_1^0 p_1^1 p_2^0 / s_1 f_1^0)$.

Subclass L19: $(s_w)^2 s_x (d)^3$, 10 determinants, degeneracy= 2.

i	Determinants	$b^{(1)}_{K\alpha}$
1	$(s_1 s_2 d_1^0 d_1^1 / s_1 d_1^0)$	$\sqrt{70}/3$

The full degenerate space is obtained by projecting, in addition, the following determinant: $(s_1 d_1^{\bar{1}} d_1^0 d_1^2 / s_1 s_2)$.

TABLE 3 continued

Subclass L20: $(s)^2 p_w p_x (d)^2$, 64 determinants, degeneracy= 11.

i	Determinants	$b_{K\alpha}^{(5)}$	$b_{K\alpha}^{(10)}$
1	$(s_1 p_1^{\bar{1}} p_2^1 d_1^1 / s_1 d_1^0)$	1.5683137	0.
2	$(s_1 p_1^{\bar{1}} p_2^0 d_1^1 / s_1 d_1^1)$	0.4527332	1.5249857
3	$(s_1 p_2^{\bar{1}} d_1^0 d_1^2 / s_1 p_1^0)$	2.5699830	1.0791262
4	$(s_1 p_2^1 d_1^{\bar{1}} d_1^0 / s_1 p_1^1)$	1.0393190	0.5576189
5	$(s_1 p_2^0 d_1^{\bar{1}} d_1^2 / s_1 p_1^0)$	3.4985711	0.8626622
6	$(s_1 p_1^0 p_2^1 d_1^0 / s_1 d_1^0)$		-0.9149914
7	$(s_1 p_1^1 d_1^{\bar{2}} d_1^1 / s_1 p_2^1)$		-0.1078328
8	$(s_1 p_1^1 d_1^{\bar{2}} d_1^2 / s_1 p_2^0)$		-0.7624929
9	$(s_1 p_1^0 p_2^0 d_1^0 / s_1 d_1^1)$		-0.5282705
10	$(s_1 p_1^1 p_2^{\bar{1}} d_1^{\bar{1}} / s_1 d_1^2)$		3.2349832

The full degenerate space is obtained by projecting, in addition, the following determinant: $(s_1 p_1^1 d_1^{\bar{1}} d_1^1 / s_1 p_2^0)$.

Subclass L21: $(s)^2 p (d)^2 f$, 118 determinants, degeneracy= 12.

i	Determinants	$b_{K\alpha}^{(1)}$
1	$(s_1 p_1^0 d_1^0 d_1^1 / s_1 f_1^0)$	4.3204938

The full degenerate space is obtained by projecting, in addition, the following determinants: $(s_1 p_1^{\bar{1}} d_1^{\bar{1}} d_1^0 / s_1 f_1^3)$, $(s_1 p_1^{\bar{1}} d_1^{\bar{1}} d_1^1 / s_1 f_1^2)$, $(s_1 p_1^1 d_1^{\bar{2}} d_1^0 / s_1 f_1^2)$, $(s_1 d_1^{\bar{2}} d_1^{\bar{1}} f_1^3 / s_1 p_1^1)$, $(s_1 d_1^{\bar{2}} d_1^1 f_1^2 / s_1 p_1^0)$, $(s_1 d_1^1 d_1^2 f_1^{\bar{3}} / s_1 p_1^1)$, $(s_1 d_1^{\bar{1}} d_1^2 f_1^0 / s_1 p_1^0)$, $(s_1 p_1^0 d_1^0 f_1^1 / s_1 d_1^0)$, $(s_1 p_1^1 d_1^0 f_1^0 / s_1 d_1^0)$, $(s_1 p_1^1 d_1^1 f_1^{\bar{2}} / s_1 d_1^1)$, $(s_1 p_1^0 d_1^2 f_1^{\bar{3}} / s_1 d_1^2)$.

TABLE 4

SLATER DETERMINANTS AND $b_{K\alpha}^{(p)}$ COEFFICIENTS OF INTERSHELL CONFIGURATIONS

Subclass I1: $s_w s_x (s_y)^2 (p)^2$, same as L2.

Subclass I2: $s_w s_x s_y s_z (p)^2$, 15 determinants, degeneracy= 6.

i	Determinants	$b_{K\alpha}^{(5)}$	$b_{K\alpha}^{(6)}$
1	$(s_1 s_2 s_3 s_4 / p_1^0 p_1^1)$	$1/\sqrt{3}$	-1
2	$(s_1 s_2 s_4 p_1^1 / s_3 p_1^0)$	-3	1
3	$(s_1 s_2 s_3 p_1^0 / s_4 p_1^1)$	-3	3
4	$(s_1 s_3 s_4 p_1^1 / s_2 p_1^0)$	0	-2
5	$(s_1 s_2 p_1^0 p_1^1 / s_3 s_4)$	3	-1
6	$(s_1 s_3 p_1^0 p_1^1 / s_2 s_4)$	0	2

Subclass I3: $s_w s_x (p)^4$, 4 determinants, degeneracy= 2.

i	Determinants	$b_{K\alpha}^{(2)}$
1	$(s_1 s_2 p_1^{\bar{1}} p_1^1 / p_1^0 p_1^1)$	$2/\sqrt{2}$
2	$(s_1 p_1^{\bar{1}} p_1^0 p_1^1 / s_2 p_1^1)$	2

Subclass I4: $s_w s_x (p_y)^3 p_z$, 27 determinants, degeneracy = 9.

i	Determinants	$b_{K\alpha}^{(8)}$	$b_{K\alpha}^{(9)}$
1	$(s_1 s_2 p_1^{\bar{1}} p_2^1 / p_1^0 p_1^1)$	$4/\sqrt{6}$	$-4/\sqrt{2}$
2	$(s_1 s_2 p_1^{\bar{1}} p_1^0 / p_1^1 p_2^1)$	6	-2
3	$(s_1 p_1^{\bar{1}} p_1^1 p_2^0 / s_2 p_1^1)$	0	6

TABLE 4 continued

Subclass I4 (continued).

i	Determinants	$b_{K\alpha}^{(8)}$	$b_{K\alpha}^{(9)}$
4	$(s_1 s_2 p_1^{\bar{1}} p_1^{1}/p_1^{1} p_2^{0})$	$9/\sqrt{6}$	$3/\sqrt{2}$
5	$(s_1 s_2 p_1^{0} p_2^{0}/p_1^{0} p_1^{1})$	5	1
6	$(s_1 s_2 p_1^{1} p_2^{\bar{1}}/p_1^{0} p_1^{1})$	10	1
7	$(s_2 p_1^{\bar{1}} p_1^{0} p_2^{1}/s_1 p_1^{1})$	0	4
8	$(s_1 s_2 p_1^{0} p_1^{1}/p_1^{1} p_2^{\bar{1}})$	6	2
9	$(s_1 p_1^{0} p_1^{1} p_2^{\bar{1}}/s_2 p_1^{1})$	0	4

Subclass I5: $s_w s_x (p_y)^2 (p_z)^2$, 46 determinants, degeneracy = 13.

i	Determinants	$b_{K\alpha}^{(7)}$
1	$(s_1 s_2 p_1^{\bar{1}} p_2^{1}/p_1^{0} p_2^{1})$	$-2/\sqrt{6}$
2	$(s_1 s_2 p_1^{0} p_2^{1}/p_1^{0} p_2^{0})$	4
3	$(s_1 p_1^{0} p_2^{0} p_2^{1}/s_2 p_1^{0})$	-2
4	$(s_1 p_1^{\bar{1}} p_1^{0} p_2^{1}/s_2 p_2^{1})$	-2
5	$(s_1 s_2 p_1^{0} p_2^{0}/p_1^{1} p_2^{0})$	6
6	$(s_2 p_1^{0} p_2^{0} p_2^{1}/s_1 p_1^{0})$	2
7	$(s_1 p_1^{0} p_1^{1} p_2^{0}/s_2 p_2^{0})$	6

The full degenerate space is obtained by projecting, in addition, the following determinants: $(s_1 s_2 p_1^{\bar{1}} p_2^{0}/p_1^{1} p_2^{1})$, $(s_1 s_2 p_2^{0} p_2^{1}/p_1^{\bar{1}} p_1^{1})$, $(s_1 p_1^{1} p_2^{0} p_2^{1}/s_2 p_1^{\bar{1}})$, $(s_1 p_1^{0} p_2^{\bar{1}} p_2^{1}/s_2 p_1^{1})$, $(s_1 p_1^{\bar{1}} p_1^{1} p_2^{0}/s_2 p_2^{1})$, and $(s_1 s_2 p_1^{1} p_2^{\bar{1}}/p_1^{0} p_2^{1})$.

TABLE 4 continued

Subclass I6: $s_w s_x (p_y)^2 \; p_z p_u$, 106 determinants, degeneracy = 27.

i	Determinants	$b_{K\alpha}^{(2)}$	$b_{K\alpha}^{(26)}$	$b_{K\alpha}^{(27)}$
1	$(s_1 s_2 p_1^{\bar{1}} p_2^1 / p_1^0 p_3^1)$	$-2/\sqrt{105}$	0	0
2	$(s_1 p_1^{\bar{1}} p_2^1 p_3^0 / s_2 p_1^1)$	21	0	$6/\sqrt{3}$
3	$(s_1 s_2 p_1^{\bar{1}} p_2^0 / p_1^1 p_3^1)$		0	6
4	$(s_2 p_1^{\bar{1}} p_2^0 p_3^1 / s_1 p_1^1)$		-12/3	-8
5	$(s_1 s_2 p_2^1 p_3^1 / p_1^{\bar{1}} p_1^0)$		13	7
6	$(s_1 s_2 p_2^0 p_3^1 / p_1^{\bar{1}} p_1^1)$		21	7
7	$(s_1 s_2 p_2^1 p_3^{\bar{1}} / p_1^0 p_1^1)$		-6	-6
8	$(s_2 p_1^{\bar{1}} p_1^1 p_2^0 / s_1 p_3^1)$		6	-2
9	$(s_2 p_1^1 p_2^1 p_3^{\bar{1}} / s_1 p_1^0)$		-15	-1
10	$(s_1 p_1^1 p_2^{\bar{1}} p_3^0 / s_2 p_1^1)$		6	4
11	$(s_1 p_1^{\bar{1}} p_1^0 p_3^1 / s_2 p_2^1)$		6	0
12	$(s_1 s_2 p_1^0 p_3^0 / p_1^1 p_2^0)$		0	6
13	$(s_2 p_1^{\bar{1}} p_1^0 p_2^1 / s_1 p_3^1)$		6	0
14	$(s_1 p_1^0 p_2^0 p_3^1 / s_2 p_1^0)$		-15	-13
15	$(s_1 p_1^1 p_2^1 p_3^{\bar{1}} / s_2 p_1^0)$		-3	-5
16	$(s_1 p_1^1 p_2^0 p_3^1 / s_2 p_1^{\bar{1}})$		-3	1
17	$(s_1 p_1^0 p_2^{\bar{1}} p_3^1 / s_2 p_1^1)$		6	-2
18	$(s_1 s_2 p_1^1 p_2^1 / p_1^{\bar{1}} p_3^0)$		-12	-2
19	$(s_2 p_1^1 p_2^0 p_3^0 / s_1 p_1^0)$		3	-1
20	$(s_1 p_1^{\bar{1}} p_1^1 p_2^0 / s_2 p_3^1)$		9	3
21	$(s_1 p_1^{\bar{1}} p_1^0 p_2^1 / s_2 p_3^1)$		3	-1

TABLE 4 continued

Subclass I6 (continued).

i	Determinants	$b_{K\alpha}^{(2)}$	$b_{K\alpha}^{(26)}$	$b_{K\alpha}^{(27)}$
22	$(s_1 p_1^{\bar{1}} p_1^1 p_3^0 / s_2 p_2^1)$		15/3	$1/\sqrt{3}$
23	$(s_1 s_2 p_1^0 p_3^1 / p_1^0 p_2^0)$		12	8
24	$(s_1 s_2 p_1^1 p_2^{\bar{1}} / p_1^1 p_3^0)$		- 6	- 4
25	$(s_2 p_1^0 p_2^{\bar{1}} p_3^1 / s_1 p_1^1)$		-27	- 9
26	$(s_1 s_2 p_1^0 p_1^1 / p_2^{\bar{1}} p_3^1)$		9	3
27	$(s_1 p_1^0 p_1^1 p_2^0 / s_2 p_3^0)$			6

Subclass I7: $s_w s_x (p)^2 (d)^2$, 100 determinants, degeneracy = 15.

i	Determinants	$b_{K\alpha}^{(7)}$
1	$(s_1 s_2 p_1^1 d_1^0 / p_1^0 d_1^0)$	$\sqrt{30}/\sqrt{3}$
2	$(s_1 p_1^{\bar{1}} p_1^1 d_1^0 / s_2 d_1^1)$	$-\sqrt{10}$
3	$(s_1 s_2 p_1^{\bar{1}} d_1^1 / p_1^0 d_1^1)$	$-\sqrt{30}$
4	$(s_1 s_2 p_1^{\bar{1}} d_1^2 / p_1^0 d_1^0)$	$-\sqrt{20}$
5	$(s_1 s_2 p_1^1 d_1^2 / p_1^{\bar{1}} d_1^{\bar{1}})$	$-\sqrt{60}$
6	$(s_1 s_2 p_1^1 d_1^1 / p_1^{\bar{1}} d_1^0)$	$-\sqrt{40}$
7	$(s_1 p_1^0 p_1^1 d_1^1 / s_2 d_1^{\bar{1}})$	$\sqrt{30}$

The full degenerate space is obtained by projecting, in addition, the following determinants: $(s_1 s_2 p_1^0 d_1^{\bar{2}} / p_1^1 d_1^2)$, $(s_1 p_1^{\bar{1}} p_1^0 d_1^0 / s_2 d_1^2)$, $(s_2 p_1^{\bar{1}} p_1^1 d_1^0 / s_1 d_1^1)$, $(s_1 s_2 p_1^{\bar{1}} d_1^0 / p_1^1 d_1^1)$, $(s_1 p_1^{\bar{1}} d_1^0 d_1^1 / s_2 p_1^1)$, $(s_1 p_1^1 d_1^{\bar{1}} d_1^2 / s_2 p_1^{\bar{1}})$, $(s_2 p_1^1 d_1^{\bar{2}} d_1^1 / s_1 p_1^1)$, $(s_1 s_2 d_1^{\bar{1}} d_1^2 / p_1^{\bar{1}} p_1^1)$.

TABLE 4 continued

Subclass I8: $(s_u)^2 s_w s_x p_y p_z$, same as L11.

Subclass I9: $(s_w)^2 s_x p_y p_z d$, same as L12.

Subclass I10: $(s_w)^2 s_x p d f$, same as L13.

TABLE 5

SLATER DETERMINANTS AND $b_{K\alpha}^{(p)}$ COEFFICIENTS OF KL SHELL CONFIGURATIONS

Subclass KL1 : $(p_w)^4 (p_x)^2$, 12 determinants, degeneracy = 5.

i	Determinants	$b_{K\alpha}^{(2)}$
1	$(p_1^{\bar{1}} p_1^0 p_1^1 p_2^1 / p_1^{\bar{1}} p_2^1)$	$-1/\sqrt{3}$
2	$(p_1^{\bar{1}} p_1^0 p_1^1 p_2^0 / p_1^1 p_2^0)$	3

The full degenerate space is obtained by projecting, in addition, the following determinants: $(p_1^{\bar{1}} p_1^1 p_2^0 p_2^1 / p_1^{\bar{1}} p_1^1)$, $(p_1^{\bar{1}} p_1^0 p_2^0 p_2^1 / p_1^0 p_1^1)$, $(p_1^0 p_1^1 p_2^{\bar{1}} p_2^0 / p_1^0 p_1^1)$.

Subclass KL2: $(p_w)^4 p_x p_y$, 28 determinants, degeneracy = 9.

i	Determinants	$b_{K\alpha}^{(7)}$
1	$(p_1^{\bar{1}} p_1^0 p_2^0 p_3^1 / p_1^0 p_1^1)$	$2/\sqrt{6}$
2	$(p_1^{\bar{1}} p_1^1 p_2^0 p_3^0 / p_1^0 p_1^1)$	6
3	$(p_1^{\bar{1}} p_1^1 p_2^1 p_3^0 / p_1^{\bar{1}} p_1^1)$	2
4	$(p_1^{\bar{1}} p_1^1 p_2^0 p_3^1 / p_1^{\bar{1}} p_1^1)$	2
5	$(p_1^{\bar{1}} p_1^0 p_2^1 p_3^0 / p_1^0 p_1^1)$	2
6	$(p_1^{\bar{1}} p_1^0 p_1^1 p_2^1 / p_1^{\bar{1}} p_3^1)$	-2
7	$(p_1^{\bar{1}} p_1^0 p_1^1 p_2^0 / p_1^1 p_3^0)$	6

The full degenerate space is obtained by projecting, in addition, the following determinants: $(p_1^0 p_1^1 p_2^{\bar{1}} p_3^1 / p_1^{\bar{1}} p_1^1)$, $(p_1^{\bar{1}} p_1^0 p_1^1 p_3^0 / p_1^0 p_2^1)$.

TABLE 5 continued

Subclass KL3: $(p)^4(d)^2$, 27 determinants, degeneracy = 6.

i	Determinants	$b_{K\alpha}^{(2)}$
1	$(p_1^{\bar{1}}p_1^0p_1^1d_1^1/p_1^{\bar{1}}d_1^1)$	$-5/\sqrt{45}$
2	$(p_1^{\bar{1}}p_1^0p_1^1d_1^0/p_1^1d_1^0)$	15

The full degenerate space is obtained by projecting, in addition, the following determinants: $(p_1^{\bar{1}}p_1^1d_1^0d_1^1/p_1^{\bar{1}}p_1^1)$, $(p_1^{\bar{1}}p_1^0d_1^0d_1^1/p_1^0p_1^1)$, $(p_1^0p_1^1d_1^{\bar{1}}d_1^0/p_1^0p_1^1)$, $(p_1^0p_1^1d_1^{\bar{2}}d_1^1/p_1^0p_1^1)$.

Subclass KL4: $s_ws_xs_y(p)^2d$, 53 determinants, degeneracy = 9.

i	Determinants	$b_{K\alpha}^{(4)}$
1	$(s_1s_2s_3d_1^2/p_1^{\bar{1}}p_1^0)$	$-25/\sqrt{3000}$
2	$(s_1s_3p_1^{\bar{1}}d_1^2/s_2p_1^0)$	$-25/\sqrt{30}$
3	$(s_1s_3p_1^{\bar{1}}p_1^0/s_2d_1^2)$	$25/\sqrt{3000}$
4	$(s_1s_3p_1^0d_1^0/s_2p_1^1)$	$\sqrt{320}/3$

The full degenerate space is obtained by projecting, in addition, the following determinants: $(s_1s_2s_3p_1^1/p_1^{\bar{1}}d_1^1)$, $(s_1s_2p_1^1d_1^1/s_3p_1^{\bar{1}})$, $(s_1s_2p_1^{\bar{1}}d_1^2/s_3p_1^0)$, $(s_2s_3p_1^1d_1^0/s_1p_1^0)$, $(s_1s_2p_1^0p_1^1/s_3d_1^0)$.

Subclass KL5: $(p_w)^3(p_x)^2p_y$, 85 determinants, degeneracy = 21.

i	Determinants	$b_{K\alpha}^{(18)}$
1	$(p_1^1p_2^{\bar{1}}p_2^0p_3^0/p_1^0p_1^1)$	$4/\sqrt{3}$
2	$(p_1^{\bar{1}}p_1^1p_2^{\bar{1}}p_3^1/p_1^1p_2^0)$	-6
3	$(p_1^{\bar{1}}p_1^1p_2^0p_3^1/p_1^1p_2^{\bar{1}})$	-6

TABLE 5 continued

Subclass KL 5 (continued).

i	Determinants	$b_{K\alpha}^{(18)}$
4	$(p_1^{\bar{1}}p_1^0p_2^0p_3^0/p_1^1p_2^1)$	$14/\sqrt{3}$
5	$(p_1^{\bar{1}}p_1^1p_2^0p_3^0/p_1^0p_2^1)$	4
6	$(p_1^{\bar{1}}p_1^0p_2^1p_3^0/p_1^1p_2^0)$	- 2
7	$(p_1^{\bar{1}}p_1^1p_2^1p_3^0/p_1^0p_2^0)$	12
8	$(p_1^{\bar{1}}p_1^1p_2^1p_3^{\bar{1}}/p_1^1p_2^0)$	- 8
9	$(p_1^{\bar{1}}p_1^0p_2^0p_3^1/p_1^1p_2^0)$	- 6
10	$(p_1^0p_2^{\bar{1}}p_2^1p_3^1/p_1^{\bar{1}}p_1^1)$	-12
11	$(p_1^0p_2^0p_2^1p_3^1/p_1^{\bar{1}}p_1^0)$	- 4
12	$(p_1^{\bar{1}}p_1^1p_2^0p_2^1/p_1^{\bar{1}}p_3^1)$	- 4
13	$(p_1^{\bar{1}}p_1^1p_2^0p_3^0/p_1^1p_2^0)$	- 3
14	$(p_1^{\bar{1}}p_1^0p_2^1p_3^0/p_1^0p_2^1)$	10
15	$(p_1^{\bar{1}}p_1^1p_2^1p_3^0/p_1^{\bar{1}}p_2^1)$	7
16	$(p_1^0p_1^1p_2^{\bar{1}}p_3^1/p_1^0p_2^0)$	8
17	$(p_1^{\bar{1}}p_1^0p_1^1p_3^1/p_2^{\bar{1}}p_2^1)$	4
18	$(p_1^0p_1^1p_2^0p_3^0/p_1^0p_2^0)$	6

The full degenerate space is obtained by projecting, in addition, the following determinants: $(p_1^0p_2^{\bar{1}}p_2^0p_3^1/p_1^0p_1^1)$, $(p_1^0p_2^{\bar{1}}p_2^1p_3^0/p_1^0p_1^1)$, $(p_1^{\bar{1}}p_1^0p_2^1p_3^1/p_1^1p_2^{\bar{1}})$.

TABLE 5 continued

Subclass KL6: $s(p_w)^2(p_x)^2 d$, 181 determinants, degeneracy= 26.

i	Determinants	$b_{K\alpha}^{(1)}$	$b_{K\alpha}^{(4)}$	$b_{K\alpha}^{(5)}$
1	$(s_1 p_1^0 p_2^0 d_1^0 / p_1^1 p_2^0)$	$\sqrt{8}$	0.779965319	0.832276131
2	$(s_1 p_1^0 p_2^0 d_1^1 / p_1^1 p_2^{\bar{1}})$		0.573125876	0.350645971
3	$(s_1 p_1^0 p_2^1 d_1^{\bar{1}} / p_1^1 p_2^0)$		0.573125876	0.350645971
4	$(s_1 p_1^{\bar{1}} p_1^1 p_2^0 / p_2^0 d_1^1)$		2.579066443	1.099556503
5	$(s_1 p_1^1 p_2^0 d_1^1 / p_1^{\bar{1}} p_2^0)$			2.870102209

i	Determinants	$b_{K\alpha}^{(8)}$	$b_{K\alpha}^{(11)}$
1		-0.800249258	0.493336795
2		-0.044509342	-0.071435955
3		-2.149303254	0.027005928
4		0.303762687	0.085555993
5		-0.650920044	-0.920828417
6	$(s_1 p_1^0 p_2^0 d_1^{\bar{1}} / p_1^1 p_2^1)$	-2.255568812	-0.766619174
7	$(s_1 p_1^0 p_2^{\bar{1}} d_1^0 / p_1^1 p_2^1)$	-3.332158754	-1.187570110
8	$(s_1 p_1^1 p_2^{\bar{1}} d_1^0 / p_1^0 p_2^1)$	3.928165571	-0.077579517
9	$(s_1 p_1^{\bar{1}} p_2^0 d_1^0 / p_1^1 p_2^1)$		-0.851584885
10	$(s_1 p_1^0 p_2^1 d_1^{\bar{1}} / p_1^1 p_2^0)$		-0.166382392
11	$(s_1 p_1^1 p_2^1 d_1^0 / p_1^0 p_2^{\bar{1}})$		3.487230624

The full degenerate space is obtained by projecting, in addition, the following determinants: $(s_1 p_1^0 p_2^{\bar{1}} d_1^2 / p_1^1 p_2^{\bar{1}})$, $(s_1 p_1^{\bar{1}} p_1^0 p_2^0 / p_2^0 d_1^2)$,

TABLE 5 continued

Subclass KL6 (continued).

$(s_1 p_1^{\bar{1}} p_2^0 d_1^2 / p_1^1 p_2^{\bar{1}})$, $(s_1 p_1^1 p_2^{\bar{1}} d_1^2 / p_1^{\bar{1}} p_2^0)$, $(s_1 p_1^0 p_2^0 d_1^1 / p_1^{\bar{1}} p_2^1)$, $(s_1 p_1^{\bar{1}} p_1^0 p_2^1 / p_2^0 d_1^1)$,
$(s_1 p_1^1 p_2^{\bar{1}} d_1^1 / p_1^{\bar{1}} p_2^1)$, $(s_1 p_2^{\bar{1}} p_2^0 d_1^1 / p_1^0 p_1^1)$, $(s_1 p_1^{\bar{1}} p_1^1 d_1^2 / p_2^{\bar{1}} p_2^0)$, $(s_1 p_1^0 p_2^{\bar{1}} p_2^0 / p_1^1 d_1^1)$,
$(p_1^0 p_2^{\bar{1}} p_2^0 d_1^2 / s_1 p_1^0)$, $(p_1^{\bar{1}} p_1^1 p_2^{\bar{1}} d_1^1 / s_1 p_2^1)$, $(p_1^{\bar{1}} p_1^1 p_2^0 p_2^1 / s_1 d_1^0)$, $(p_1^0 p_1^1 p_2^1 d_1^{\bar{2}} / s_1 p_2^1)$,
$(s_1 p_1^0 p_1^1 p_2^0 / p_2^0 d_1^0)$.

and L shells (they are denoted by L1 K1, ..., L10 K10); for L1 through L9, the projection corresponding to the largest value of the superscript (p), always belongs to the coupling $^1S(s_w)^2\ ^1S(xy)\ ^3P(p_1)^2$. The other projections correspond to less obvious, or linear combinations of, internal couplings. Table 4 contains the subclasses of the Intershell excitations: the only reported element of I3, I5, and I7, corresponds to $^1S(s_1 s_2)\ ^1S(x)^2\ ^3P(p_1)^2$, while for I2, I4, and I6, the two elements in the table belong to $^1S\{^3S(s_1 s_2)\ ^3S(xy)\}\ ^3P(p_1)^2$ and $^1S(s_1 s_2)\ ^1S(xy)\ ^3P(p_1)^2$, in that order. In Table 5, the subclasses from which only KL triple and quadruple (and larger) excitations can be obtained, are reported; for KL1, KL2, KL3, and KL5, the couplings are of the same type as in the HF configuration: $^1S(p_x)^2\ ^1S(p_1)^2\ ^3P(p_1)^2$, $^1S(p_x p_y)\ ^1S(p_1)^2\ ^3P(p_1)^2$, $^1S(d)^2\ ^1S(p_1)^2\ ^3P(p_1)^2$, and $^1S(p_x)^2\ ^1S(p_1 p_y)\ ^3P(p_1)^2$, respectively.

Only about a half of all the subclasses for which the best possible partition of the degenerate space was obtained, appear in the final CI expansion, and are reported here.

5.5. The Search for the Terms

As mentioned in Section 5.2, the three large divisions of the CI expansion, K shell, L shell, and Intershell excitations, are quite independent of each other, inasmuch as the partial energies and eigenvector components of one of them are not appreciably affected by the presence of the other two. The K shell, L shell, and Intershell CI expansions are, hence, investigated first independently; the best energies obtained for each of them are indicated in Table 6, together with the energies of their most relevant truncations. The last column of Table 6 gives the error in the truncations, as estimated from the search by adding all the partial energies of the terms which were discarded (this estimate is usually good to within 10 per cent).

Let us consider the L shell. The search has to be done by parts, according to the limitations of the computer program, as indicated in Section 5.1. At this early stage, it is not necessary to set the tolerances in the eigenvector components and the partial energies, very low; we are interested mainly, in obtaining a rough approximation to the value of the partial energy contribution of each term: we use EIG=0.0035 and TOL=0.000080 a.u.

The K shell CI search consists of approximately 720 terms. The convergence is good, and the final K shell CI expansion contains 49 terms. This is much more than the necessary number of terms when a K shell NRO basis is used; yet, it does not compare so unfavorably with the K shell CI expansion obtained for Be, with a KL shell NSO basis:(20) the main disadvantage lies in its effect on the convergence of the KL triple and quadruple excitations.

The search of the Intershell configurations yields a large number of terms, whose contributions are small but not negligible.

TABLE 6

STEPS IN THE CONFIGURATION SEARCH

Wave Function	Number of Terms	Energy	Truncation Error
L shell: best expansion	179	-37.78560	-.000400
L shell: only HF interacting terms	83	-37.78222	
L shell: EIG = 0.01, TOL = 0.000065	51	-37.78360	
L shell: EIG = 0.01, TOL = 0.000150	39	-37.78231	
K shell: best expansion	49	-37.72985	-.000035
Intershell: best expansion	110	-37.69957	-.000450
K shell Intershell: best expansion	159	-37.74080	-.000485
K shell L shell: best expansion	215	-37.82437	-.000435
K shell L shell Intershell triple and quadruple KL excitations (final wave function)	234	-37.83378	-.002400
Full CI: 7s, 6p, 4d, 3f orbital basis (estimate)		-37.8362	

The search is slowed down by the occurrence of large degeneracies; this limits the size of the secular equation, as explained in Section 5.1: for example, when searching the 27-degenerate subclass, $s_1 s_2 (p_1)^2 p_x p_y$, the maximum number of terms which can be introduced at one time is 4000/27 , i.e. 148. The total truncation error in this case, has been computed by adding the following partial energies:

$(s_1 s_2) \rightarrow$	$d_x d_y$	-.000300
$(s_1 s_2) \rightarrow$	$(f)^2, f_x f_y$	-.000100
$(s_1 s_2) \rightarrow$	others	-.000025
$(s_1 p_1) \rightarrow$	all	-.000025

When the K shell and Intershell expansions are put together, the results are remarkably additive. This does not happen, however, when the K and L shell expansions are combined: in this case, although the partial energies of the K shell excitations do not change much, those of the L shell ones are substantially diminished. The total energy loss by non-additivity is about -.0025 a.u., and it is partially recovered when the triple and quadruple excitations involving both the K and L shells, are introduced.

Finally, all three expansions, and the triple and quadruple KL excitations are lumped together into a final search, to obtain the total wave function. The corresponding truncation error reported in Table 6, is calculated by adding the following partial energies:

K and L shell truncations	-.000943
Intershell truncations	-.000645
Triple and quadruple KL truncations	-.000315
Triple and quadruple KL from subclasses not considered	-.000500

5.6. Results

Our final CI wave function consists of 234 terms formed from a determinantal space of dimension 4836. Its corresponding energy eigenvalue is $E = -37.83378$ a.u.

The eigenvector component of the HF configuration is 0.972691373. The rest of the wave function is displayed in Tables 7 through 18.

The first seven of these tables contain excitations of the L shell alone. All the HF interacting $(s_2)^2$ excitations appearing in Table 7 belong to the coupling $^1S(s_1)^2\,^1S(xy)\,^3P(p_1)^2$. The HF non-interacting excitations are significant only for the pairs $(s_2)^2$ and s_2p_1. In these cases, and also in Tables 13 and 18, the partial energies are computed with respect to Φ_{TR}; all the others are given with respect to Φ_{HF}. The last six terms of Table 12 have zero or positive partial energies; the corresponding values with respect to Φ_{TR} are: -.000083, -.000102, -.000043, -.000032, -.000030, and -.000020 a.u., respectively.

TABLE 7

EXPANSION OF HF INTERACTING $(s_2)^2$ EXCITATIONS

Configuration[a]	Degenerate Element[b]	Eigenvector	Partial Energy[c]
$(p_1)^2$		.130723807	-15401
p_1p_2	3	-.038569453	- 2371
$(d_1)^2$	6	-.032093068	- 3779
$(s_3)^2$		-.030227981	- 2759
p_1p_3	3	.022263542	- 1370
$(p_2)^2$	5	-.018990747	- 1074
$(f_1)^2$	6	-.009298258	- 750
$(d_2)^2$	6	-.005675494	- 313
$(s_4)^2$		-.004830124	- 177
$(p_3)^2$	5	-.004305142	- 167
p_2p_3	8	.003742989	19
p_2p_4	8	.003022259	- 151
$(f_2)^2$	6	-.002914846	- 149
d_1d_2	10	-.001767170	- 110
p_2p_5	8	-.001006853	- 14
$(p_4)^2$	5	-.000976456	- 38
$(s_5)^2$		-.000478943	- 22

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a. Only the excited (i, ℓ) indices are shown.
b. The ordering of the degenerate elements is given in Table 3.
c. In units of 10^{-6} a.u.(C).

TABLE 8

EXPANSION OF HF NON-INTERACTING $(s_2)^2$ EXCITATIONS

Configuration	Degenerate Element	Eigenvector	Partial Energy
$(d_1)^2$	2	-.011214131	- 435
$(p_2)^2$	4	.010811795	- 332
p_1f_1		.007551306	- 202
$(p_2)^2$	3	-.007454889	- 140
$(d_1)^2$	5	-.007170236	- 181
$(d_1)^2$	3	-.006593000	- 142
s_3d_1	2	-.005423758	- 83
s_3d_2	3	-.004096498	- 72
$(d_1)^2$	4	-.003030145	- 29
p_1p_2	2	-.002673776	- 14
d_1d_2	5	.002190747	- 23
$(f_1)^2$	5	.002039872	- 26
$(d_2)^2$	2	-.001747914	- 20
$(p_3)^2$	4	.001610092	- 15
p_2f_1	1	-.001590192	- 10
$(f_1)^2$	3	-.001533352	- 16
d_1d_2	8	.001491326	- 16

TABLE 9

EXPANSION OF HF INTERACTING (s_2p_1) EXCITATIONS

Configuration	Degenerate Element	Eigenvector	Partial Energy
s_3p_2	3	.054006778	- 7130
s_3p_2	2	.043082303	- 4702
d_1f_1	6	.023381234	- 2950
p_2d_1	6	.017014787	- 912
p_3d_1	6	-.015566722	- 1121
d_1f_1	5	-.015280189	- 1314
p_2d_2	6	-.012395997	- 957
p_2d_1	5	.010074992	- 245
p_3d_1	5	-.008357891	- 287
p_2d_2	5	-.008274255	- 444
s_4p_3	3	-.007624900	- 436
s_4p_3	2	-.005580601	- 212
d_2f_2	6	-.005286835	- 325
d_2f_2	5	.004135588	- 211
p_4d_2	6	.002770989	- 157
s_4p_2	3	.002725362	114
s_3p_3	2	.002670829	- 128
d_2f_1	6	-.001611094	- 72
s_3p_4	2	.001520327	- 45

TABLE 9 continued

Configuration	Degenerate Element	Eigenvector	Partial Energy
s_3p_4	3	-.001148072	- 29
p_4d_2	5	.000947765	- 24
s_4p_4	2	-.000788093	- 22
s_5p_4	2	-.000474289	- 16

TABLE 10

EXPANSION OF HF NON-INTERACTING (s_2p_1) EXCITATIONS

Configuration	Degenerate Element	Eigenvector	Partial Energy
d_1f_1	4	.008633712	- 297
p_2d_2	4	.005821690	- 130
d_1f_1	3	.002426237	- 30
p_2d_2	2	-.002187318	- 21

TABLE 11

EXPANSION OF $(p_1)^2$ EXCITATIONS

Configuration	Degenerate Element	Eigenvector	Partial Energy
$(p_2)^2$		-.043150565	- 3682
$(d_1)^2$		-.034767021	- 3886
$(f_1)^2$		-.007932459	- 400
$(d_2)^2$		-.006720458	- 276
$(p_3)^2$		-.004568322	- 140
$(f_2)^2$		-.001929488	- 49

TABLE 12

EXPANSION OF L SHELL SINGLE EXCITATIONS

(s_2) Excitations.

Configuration	Degenerate Element	Eigenvector	Partial Energy
d_1	3	-.119215608	-28194
d_1	2	-.069525439	- 6399
s_3	1	.034055087	- 1432
s_4	1	.013427695	- 148
s_3	2	.009018988	0
d_2	3	-.005997222	536
d_2	2	-.004227473	166
s_5	1	-.001661924	11
s_6	1	-.001289931	4

(p_1) Excitations.

Configuration	Degenerate Element	Eigenvector	Partial Energy
p_2		.005957327	0

TABLE 13

EXPANSION OF TRIPLE AND QUADRUPLE L SHELL EXCITATIONS

$s_2(p_1)^2$ Excitations .

Configuration	Degenerate Element	Eigenvector	Partial Energy
$(d_1)^3$	1	.006633999	- 173
$(p_2)^2 d_1$	3	.005962582	- 123
$(p_2)^2 d_1$	2	.003630582	- 40
$s_3p_2p_3$	3	-.002483294	- 30
$s_3p_2p_3$	2	-.002092872	- 21
$s_4(p_2)^2$	2	-.001821914	- 16

$(s_2)^2 p_1$ Excitations .

Configuration	Degenerate Element	Eigenvector	Partial Energy
$s_3p_2d_1$	6	-.004220961	- 67
$(s_3)^2 p_2$		-.003809827	- 33
$p_2(d_1)^2$	10	.002476778	- 23
$s_3s_4p_2$	2	.002412882	- 22
$p_2(d_1)^2$	5	-.002142162	- 19
$(s_3)^2 p_3$		.002116743	- 19
$(p_2)^3$	1	.001848937	- 13
$(p_2)^2 p_3$	8	-.001839479	- 16

TABLE 13 continued

$(s_2)^2 p_1$ Excitations (continued).

Configuration	Degenerate Element	Eigenvector	Partial Energy
$(d_1)^2 f_1$	1	-.001794829	- 17

$(s_2)^2 (p_1)^2$ Excitations .

Configuration	Degenerate Element	Eigenvector	Partial Energy
$(s_3)^2 (p_2)^2$		.003620671	- 58

TABLE 14

EXPANSION OF $(s_1)^2$ EXCITATIONS

Configuration	Degenerate Element	Eigenvector	Partial Energy
$(p_4)^2$	5	-.010578751	- 6996
p_3p_4	8	-.009548171	- 4128
$(s_5)^2$		-.008621388	- 6863
s_4s_5	2	-.007052000	- 2845
p_2p_4	8	-.006718510	- 1832
p_4p_5	8	-.005810230	- 4225
s_3s_5	2	.005628016	- 1651
p_2p_3	8	-.005515289	- 898
$(p_3)^2$	5	-.005166094	- 887
s_3s_4	2	.004672690	- 683
$(d_3)^2$	6	-.004532230	- 2554
$(p_5)^2$	5	-.003895650	- 2530
p_1p_4	3	-.003827283	- 573
$(s_4)^2$		-.003680683	- 491
p_1p_3	3	-.003322031	- 304
$(p_2)^2$	5	-.003017023	- 239
$(s_3)^2$		-.002982826	- 244
p_1p_2	3	-.002552750	- 162
s_3s_6	2	.002126254	28

TABLE 14 continued

Configuration	Degenerate Element	Eigenvector	Partial Energy
p_3p_5	8	-.002058667	- 482
s_4s_6	2	-.001958731	69
$(s_6)^2$		-.001732786	- 411
$(f_3)^2$	6	-.001523276	- 650
$(d_4)^2$	6	-.001283660	- 596
p_4p_6	8	-.001239151	173
$(p_6)^2$	5	-.001212527	- 537
d_2d_3	10	-.001072814	- 97
s_5s_7	2	.001069407	72
s_5s_6	2	-.001057058	373
p_3p_6	8	-.000799082	- 1
p_2p_5	8	-.000741025	- 99
$(p_1)^2$		.000722793	- 16
s_4s_7	2	.000543591	- 13
d_1d_3	10	.000499335	- 19
$(s_7)^2$		-.000367178	- 96
p_1p_5	3	-.000355210	- 25
p_5p_6	8	.000299144	- 143

TABLE 15

EXPANSION OF (s_1) EXCITATIONS

Configuration	Degenerate Element	Eigenvector	Partial Energy
d_1	3	.003580933	- 183
d_2	3	-.002892015	- 125
s_3	1	-.002339943	- 72
s_4	1	.001284268	- 25
d_2	2	-.001216549	- 22
d_3	2	.000577873	- 20

TABLE 16

EXPANSION OF $(s_1 s_2)$ EXCITATIONS

Configuration	Degenerate Element	Eigenvector	Partial Energy
p_1p_2	9	-.004669457	- 312
p_1p_3	8	-.004322516	- 365
p_2p_4	26	-.004273199	- 533
p_1p_4	8	-.003608779	- 408
$(p_2)^2$	7	.003568234	- 179
p_2p_3	26	-.003448177	- 226
p_3p_4	26	-.002988004	- 263
p_2p_3	27	.002811528	- 129
$(s_5)^2$	2	-.002805974	- 665
p_1p_3	9	-.002755666	- 143
s_4s_5	6	-.002730652	- 340
s_3s_4	6	.002619509	- 122
$(p_1)^2$	2	-.002603988	- 92
$(p_4)^2$	7	-.002523425	- 353
p_1p_2	8	-.002192258	- 87
p_4p_5	27	-.001976463	- 405
$(s_4)^2$	2	-.001739677	- 71
s_3s_5	6	.001660794	- 156
$(s_3)^2$	2	-.001591106	- 43

TABLE 16 continued

Configuration	Degenerate Element	Eigenvector	Partial Energy
p_3p_4	27	-.001439866	- 83
$(d_2)^2$	7	-.001354707	- 32
$(d_1)^2$	7	-.001165515	- 16
s_4s_6	6	-.001051689	16
$(p_5)^2$	7	-.001034600	- 181
p_4p_5	26	-.000879486	- 65
p_3p_5	27	-.000795788	- 58
$(d_3)^2$	7	.000689309	- 53
s_5s_6	6	-.000684705	73
$(s_6)^2$	2	-.000639710	- 40
p_2p_5	27	-.000629025	- 26
s_3s_5	5	-.000547538	- 15
p_4p_6	27	-.000367892	21
$(p_6)^2$	7	-.000325176	- 39
$(d_4)^2$	7	.000306196	- 32
p_5p_6	27	.000165226	- 24

TABLE 17

EXPANSION OF (s_1p_1) EXCITATIONS

Configuration	Degenerate Element	Eigenvector	Partial Energy
p_3d_2	6	.004563477	- 405
p_2d_1	6	-.004451068	- 336
p_3d_1	6	-.004377461	- 395
s_3p_3	2	.004264900	- 314
p_2d_2	6	.004106014	- 272
s_3p_2	2	.003652877	- 206
p_4d_2	6	.003157288	- 321
s_3p_4	2	.002926388	- 251
s_4p_3	2	-.002810999	- 163
s_4p_4	2	-.002582116	- 218
p_4d_1	6	-.002575422	- 232
p_4d_3	6	-.002544174	- 429
s_4p_2	2	-.002257406	- 89
s_5p_4	2	-.001978537	- 205
p_3d_3	6	-.001492484	- 116
p_2d_2	5	.001438683	- 32
s_5p_3	2	-.001219349	- 54
s_6p_4	2	-.001181885	- 44
p_3d_3	5	-.001002019	- 63

TABLE 17 continued

Configuration	Degenerate Element	Eigenvector	Partial Energy
d_2f_1	6	.000984567	- 19
p_2d_3	5	-.000932689	- 52
d_2f_2	6	.000931386	- 20
p_4d_3	5	-.000899235	- 58
s_6p_3	2	-.000884990	- 26
p_4d_4	6	-.000831561	- 47
p_3d_2	5	.000820465	- 12
d_3f_2	6	-.000630841	- 27
p_2d_3	6	-.000612143	- 25
p_3d_4	6	-.000571633	- 25
p_5d_3	6	-.000552256	- 55
d_3f_3	6	-.000532533	- 52
d_3f_3	5	.000384394	- 27
s_5p_5	2	-.000378560	- 27
s_5p_2	2	-.000305469	- 8

TABLE 18

EXPANSION OF TRIPLE AND QUADRUPLE KL SHELL EXCITATIONS

$(s_1)^2(s_2)^2$ Excitations .

Configuration	Degenerate Element	Eigenvector	Partial Energy
$(p_1)^2(p_4)^2$	2	-.001462661	- 125
$(p_1)^2 p_3p_4$	7	-.001328775	- 76
$(s_5)^2(p_1)^2$		-.001039978	- 106
$(p_1)^2 p_2p_4$	7	-.000901142	- 30
$s_4s_5(p_1)^2$	2	-.000771583	- 40
$(p_1)^2(p_3)^2$	2	-.000734083	- 16
$(p_1)^2 p_2p_3$	7	-.000725990	- 15
$(p_1)^2 p_4p_5$	7	-.000688048	- 64
$s_3s_4(p_1)^2$	2	.000661616	- 12
$(p_1)^2(d_3)^2$	2	-.000621451	- 45
$s_3s_5(p_1)^2$	2	.000595050	- 22
$p_1p_2(p_4)^2$	18	.000553192	- 14
$(p_1)^2(p_5)^2$	2	-.000516001	- 43
$(p_1)^2 p_3p_5$	7	-.000207359	- 6
$(p_1)^2 p_5p_6$	7	.000091817	- 6
$s_5s_6(p_1)^2$	2	-.000080621	4

TABLE 18 continued

$(s_1)^2 s_2$ Excitations .

Configuration	Degenerate Element	Eigenvector	Partial Energy
$(s_5)^2 d_1$	3	-.000925887	- 87
$(p_4)^2 d_1$	8	-.000824538	- 34
$(p_4)^2 d_1$	4	.000756670	- 28
$(p_4)^2 d_1$	11	-.000734064	- 27
$(p_4)^2 d_1$	5	-.000630004	- 20
$s_4 s_5 d_1$	4	.000611896	- 25
$(p_4)^2 d_1$	1	.000601056	- 18
$(s_5)^2 d_1$	2	-.000540972	- 30
$s_3 s_5 d_1$	4	-.000480622	- 14

$(s_1)^2 s_2 p_1$ Excitations .

Configuration	Degenerate Element	Eigenvector	Partial Energy
$s_3 p_2 (p_4)^2$	2	.000624209	- 20
$s_3 (s_5)^2 p_2$	3	-.000423153	- 18

$(s_1)^2 (p_1)^2$ Excitations .

Configuration	Degenerate Element	Eigenvector	Partial Energy
$(p_2)^2 (p_4)^2$	5	.000579111	- 17

The Intershell expansion (Tables 16 and 17) is slowly convergent; all its terms are HF interacting.

Table 18 shows the triple and quadruple excitations which involve orbitals of both shells. The $(s_1)^2(s_2)^2$ excitations preserve the ${}^1S$, ${}^1S$ coupling of the original orbitals, while the only occurring $(s_1)^2(p_1)^2$ excitation maintains a ${}^3P$ through the scheme ${}^1S(p_4)^2$ ${}^3P(p_2)^2$.

As mentioned in Chapter II, it can be seen from the tables that a close agreement exists between the eigenvector components of the triple and quadruple excitations, and the products of the eigenvector components of the single and double excitations from which they can be formed.

CHAPTER VI

DISCUSSION

The interpretation and utilization of the results obtained, involves three main areas of interest, namely, (i) the energy, (ii) the analysis of the wave function in terms of constituents which are transferable from one system to another, and, (iii) the computation of properties such as those mentioned in the Introduction.

We shall here discuss in detail only the first of these points. The second problem, (ii), is presently being investigated: in the next section, the tranferability, within chemical accuracy, of K shells, shall be shown. The systematic investigation of the third problem, (iii), concerns not only the computation of average values, but also the determination of how the latter are affected by various truncations of the wave function. For example, since the electronic spin density at the nucleus depends only on the eigenvector components of the K shell single excitations (Table 13), one may look for a way to truncate the total wave function, which leaves this part invariant.

6.1. The Correlation Energy

It is very common practice to talk of the energy results in terms of the percentage of correlation energy (CE) obtained. However, since the definition of CE involves the total non-relativistic energy, which is not well-known, its use as a "yardstick" in which to measure the goodness of wave functions has to be made with some reservation.

Clementi has estimated the CE of the ^3P state of C to be 0.158 a.u.(38) This value is obtained by computing the average value of a simplified relativistic Hamiltonian, with respect to the HF wave function. The CE shall be estimated here on the basis of our calculation and of a study of the errors involved in the various truncations.

The difference between the CE of the K shell of C and that of C^{4+}, is due mainly to the following effects: (i) the exclusion of the s_2 orbital from the expansion of the K shell of C, which amounts to 0.00257 a.u. (see Table 19); (ii) the partial exclusion of the p_1 orbital from the K shell expansion of C, due to the presence of the $(p_1)^2$ pair in the L shell (about 0.00059 a.u.); and (iii) the absence, from the C^{4+} K shell expansion, of the s_1 single excitations which appear in the corresponding C wave function, due to the fact that they do not preserve the ^1S coupling of the K shell. This energy effect (about 0.00045 a.u.) opposes those of (i) and (ii).

TABLE 19

ANGULAR ENERGY LIMITS FOR C^{4+}

	s	sp	spd	spdf	spdfg	E(total)
Weiss[a]	-32.37622	-32.40119	-32.40442	-32.40520	-32.40540	
Present orbital basis		-32.40089		-32.40461		
Same with s_2 excluded				-32.40204		
Reference 34	-32.376286	-32.401336	-32.404655			
"Exact"	-32.376289[b]	-32.401344[b]	-32.404679[b]	-32.40557[b]	-32.40588[b]	-32.40625[c]
E_{HF}[d]	-32.361154					

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a. A. W. Weiss, Phys. Rev. 122, 1826 (1961).

b. Reference 34, upper bounds estimated from rates of convergence of NSO's expansions.

c. C. L. Pekeris, Phys. Rev. 112, 1649 (1958).

d. Reference 4.

Assuming, then, that all the difference between the CE's of the K shells of C and C^{4+} can be accounted for, their errors should be the same: the total error in C^{4+} is obtained in Table 19 on the basis of the angular energy limits.

The calculation of the error in the L shell CE is done in an entirely different manner. The error due to the truncation of the L shell CI expansion is evaluated by adding the partial energies of the terms which were dropped during the search. The effect of g-, h-, and higher symmetry orbitals is estimated for each electron pair, according to an empirical procedure developed by Bunge,(34) which gives very accurate predictions for the case of the He isoelectronic series. It is illustrated in Table 20 for the $(s_2)^2$ excitations. It is based on the existence of a general pattern for the contributions $e(i, \ell)$ of the different orbitals (i, ℓ) to the energy, when these are written in the manner shown in Table 20. The energy $e(i, \ell)$ is obtained by adding the partial energies of the excitations in which (i, ℓ) occurs; only those excitations of (i, ℓ) are considered, in which (i, ℓ) occurs paired with itself or with another orbital (i', ℓ') for which $e(i', \ell') > e(i, \ell)$. One finds that:

a) $e(i, \ell+1) < e(i, \ell)$

b) $e(i, \ell+1) > e(i+1, \ell)$

c) the vertical ratios $e(i, \ell)/e(i+1, \ell)$ usually decrease smoothly for a given i value, for increasing ℓ.

Once a few of the $e(i, \ell)$'s have been obtained, the remaining

TABLE 20

DIAGRAM TO ESTIMATE $e(i, \ell)$ VALUES FOR $(s_2)^2$ EXCITATIONS

$d_1=4100$[a]					
$d_2= 580$	$f_1=1000$				
$d_3= 20$	$f_2= 150$	$g_1= 300$			
$d_4= 0$	$f_3= 10$	$g_2= 70$	$h_1= 180$		
.	$f_4= 0$	$g_3= 5$	$h_2= 30$	$i_1= 100$	
.	.	$g_4= 0$	$h_3= 1$	$i_2= 15$	. . . .
.	.	.	.	.	. . . .

---

a. In units of 10^{-6} a.u. (C).

ones are predicted according to the rules indicated above: in this way, we have estimated the effect of the g-, h-, and higher orbitals on the expansion of $(s_2)^2$, to be of the order of 0.0010 a.u. Analogously, we find 0.00045 a.u. and 0.0030 a.u. for the pairs $(p_1)^2$ and s_2p_1, respectively.

For the Intershell, similar arguments lead to an estimate of the error in the CE, of 0.00020 a.u.

Finally, all the errors are combined as described in Table 21, to give CE = -0.1546 ± 0.0010 a.u.

6.2. Comparison with other Works

As compared with the enormous amount of literature on the ground state of Be, there is indeed very little published on the ground state of C. In Table 22, we have given the results for $C(^3P)$, of variational calculations which go beyond the HF approximation. Since some of them are concerned only with the L shell CI expansion, the energy results for both the latter and the total CI wave function are displayed.

Boys's calculation (39) is the first extensive CI work on C. Weiss' emphasis is related to the computation of transition probabilities, (8) rather than the determination of wave functions: most of the improvement of our L shell expansion over his, comes from the partition of degenerate spaces. Bagus and Moser (40) perform a multiconfiguration self-consistent field calculation, aiming at the

TABLE 21

ESTIMATE OF THE TOTAL NON-RELATIVISTIC ENERGY

	Energy
Full CI estimate[a]	-37.83620
K shell error = K shell error C^{4+}	- .00165
L shell and Intershell spdf saturation[c] remainders	- .00067
Contributions of g-, h-, and higher symmetry orbitals to $(s_2)^2$ excitations	- .00100
Same, to $(p_1)^2$ excitations	- .00045
Same, to (s_2p_1) excitations	- .00300
Same, to Intershell excitations	- .00020
Total non-relativistic energy (estimate)	-37.84317
HF energy[d]	-37.68861
Correlation energy (estimate)	- .1546 ± .0010

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a. See Table 6.
b. See Table 19.
c. See Section 5.2.
d. Reference 4.

TABLE 22

CI CALCULATIONS OF C GROUND STATE

	L Shell CI			Total Wave Function		
	Basis	Terms	Energy	Basis	Terms	Energy
Bagus and Moser[a]	2s, 2p, 1d	4	-37.71485			
Boys[b]				4s, 3p, 1d	15	-37.747
Weiss[c]	4s, 3p, 2d, 2f	40	-37.77888			
This calculation (truncation)	4s, 4p, 2d, 2f	39	-37.78231			
This calculation (best)	5s, 4p, 2d, 2f	179	-37.78560	7s, 6p, 4d, 3f	234	-37.83378

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a. Reference 40.
b. Reference 39.
c. Reference 8.

obtaining of a compact representation of a CI wave function which is restricted both in the type of configurations involved and in the internal couplings allowed.

In Table 23, we have given the partition of the calculated CE in terms of the ε parameters of HF orbitals or of pairs of HF orbitals: these are defined as the sum of the partial energies of the corresponding excitations, for example $\varepsilon(s_2, p_1) = \Sigma\ E_{Kp}$, where the summation goes over all the $(s_2 p_1)$ excitations.

McKoy and Sinanoglu (41) have made estimates of pair correlation energies, using the many-electron theory.(24) Their results correspond to a different partition of the CE, but some fragments can, however, be compared with ours: in particular, their $\varepsilon(2s^2) = -.0150$ a.u., is equivalent to our contribution from the configuration $(s_1)^2(p_1)^4$. Also, their combined pair correlation energies $\varepsilon(2p \rightarrow 1s^2\ 2s^2) + \varepsilon(2p^2)$, which amount to -.0851 a.u., is closely related to our $\varepsilon(s_2, p_1) + \varepsilon(s_1, p_1) + \varepsilon(s_2) + \varepsilon(p_1, p_1)$ which gives -.0655 a.u.

6.3. Conclusions

The results obtained for the ^3P state of the carbon atom have surpassed even our most optimistic expectations. Although different states of different atoms may present new difficulties, several problems have been approached here, which are of a general nature.

The three main aspects of our calculation are: (i) the opti-

TABLE 23

PARTITION OF THE CALCULATED CORRELATION ENERGY

	Energy
E_{HF}[a]	-37.688547
$\varepsilon(s_2, s_2)$	- .028626
$\varepsilon(s_2, p_1)$	- .021625
$\varepsilon(p_1, p_1)$	- .008433
$\varepsilon(s_2)$	- .035456
$\varepsilon(s_1, s_1)$	- .040575
$\varepsilon(s_1)$	- .000447
$\varepsilon(s_1, s_2)$	- .005446
$\varepsilon(s_1, p_1)$	- .004623
E(total)	-37.833778

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a. Reference 25.

mization of the STO basis, together with the evaluation of the saturation remainders; (ii) the simplification of the description of the full CI expansion by means of NRO's; (iii) the optimum partition of the degenerate spaces, which is especially significant for open shell systems.

Because the relativistic corrections have not been considered in this work, a comparison between our energy results and the "experimental" energy $E_{exp.}$ is of doubtful significance. The latter can be found by adding the "experimental" values for the successive ionization potentials of carbon,(42) except for the ionization potential of C^{4+}, which is given more accurately by the theoretical work of Pekeris(43): we find $E_{exp.} = -37.85638 \pm 0.00002$ a.u.(C).

With a large electronic computer, it seems possible to obtain results of comparable accuracy, in short periods of time. The computation of the 1-matrix of our wave function is under way. We plan to calculate next the other two states of C arising from the HF configuration $(s_1)^2(s_2)^2(p_1)^2$, namely, the lowest ^1D and ^1S states; the corresponding wave functions will be used to obtain relativistic corrections to the energy, hyperfine constants, and other properties.

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BIOGRAPHICAL SKETCH

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June 1968

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